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Insights into the behaviour of S, F, and Cl at Santiaguito Volcano, Guatemala, from apatite and glass

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ABSTRACT

The mineral apatite can incorporate all of the major magmatic volatile species into its structure. Where melt inclusions are not available, magmatic apatite may therefore represent an opportunity to quantify volatile concentrations in the pre-eruptive melt. We analysed apatites and matrix glasses from andesites and dacites erupted from Santiaguito Volcano, Guatemala, between the 1920s and 2002. X-ray mapping shows complex zoning of sulphur in the apatite grains, but typically with sulphur-rich cores and sulphur-poor rims. Apatite microphenocrysts are enriched in F and depleted in Cl relative to inclusions. Matrix glasses are dacite to rhyolite and contain low F but up to 2400 ppm Cl. Overall, the data are consistent with progressive depletion of Cl in the most evolved melts due to crystallisation and degassing. In the absence of pristine melt inclusions, we used apatite, together with published partitioning data, to reconstruct the likely volatile contents of the pre-eruptive melt, and hence estimate long-term average gas emissions of SO₂, HF and HCl for the ongoing eruption. The data indicate time-averaged SO₂ emissions of up to 157 tonnes/day, HCl of 74–1382 tonnes/day and up to 196 tonnes/day HF. Apatite may provide a useful measure of long-term volatile emissions at volcanoes where direct emissions measurements are unavailable, or for comparison with intermittent gas sampling methods. However, significant uncertainty remains regarding volatile distribution coefficients for apatite, and their variations with temperature and pressure.

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1. Introduction

The exsolution of dissolved magmatic volatiles into bubbles during magma ascent and eruption is one of the most important processes affecting the physical properties of any volcanic system. Whereas H₂O and CO₂ are the most important volatiles by volume, S, F and Cl can have significant environmental consequences on a local to global scale, with relevance to atmospheric chemistry, human health, and ecology (e.g. Allen et al., 2000; Martin et al., 2009; Robock, 2000). Constraining the fluxes of these volatiles is an important means to assess the current and past impact of volcanic activity on the Earth's surface environment. In the absence of direct measurements of gas emissions, the volatile contents of melt inclusions, trapped in phenocrysts and isolated at depth, are routinely used to infer pre-eruptive melt volatile concentrations (e.g. Bouvier et al., 2008; Edmonds et al., 2001; Humphreys et al., 2008; Wallace, 2005). Comparison of these pre-eruptive volatile concentrations with those preserved in the matrix glass gives a petrologic estimate of volatiles degassed during volcanic eruptions (Devine et al., 1984; Thordarson et al., 1996).

However, in some magmas, melt inclusions may only be present in phases that are liable to leak or degas, or they may be present but too small for analysis, or have undergone devitrification or significant post-entrapment modification. In such cases, an alternative method for assessment of pre-eruptive volatile contents is required. Here we explore and evaluate the potential use of apatite in place of melt inclusions, to infer pre-eruptive concentrations of S, F and Cl in the magmatic liquid at Santiaguito volcano, Guatemala, commenting on the advantages and limitations of the method. This work builds on previous studies, for example at Huaynaputina, Peru (Dietterich and de Silva, 2010) and Irazú volcano, Costa Rica (Boyce and Hervig, 2009). We use the data to infer pre-eruptive volatile concentrations in magmas erupted from Santiaguito volcano, and hence estimate the time-averaged gas emissions of this long-lived, but poorly monitored, volcanic dome complex.

2. Geological background and petrology

Activity at the silicic lava dome complex of Santiaguito, Guatemala, began in 1922 and continues at the time of writing (2015). The dome sits on the shoulder of the much older Santa María volcanic edifice, which in 1902 was the site of a major bimodal explosive eruption, dominated by dacite pumice. Activity at the Santiaguito edifice is

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characterized by extrusion of lava domes and flows, with regular explosive release of gas and ash (Bluth and Rose, 2004; Escobar Wolf et al., 2010; Rose, 1972, 1987), and substantial passive degassing between explosions (Holland et al., 2011). Persistent cloud cover, challenging terrain, and the explosive nature of the volcanic activity have limited the measurement of volatile emissions using satellite- or ground-based remote sensing methods or direct techniques (Santa María Volcano Observatory written records; Holland et al., 2011; Rodriguez et al., 2004). However, previous work indicates that the effusive eruption of Santiaguito should result in significant halogen output in the volcanic plume as a result of open-system degassing (Balcone-Boissard et al., 2010; Villemant et al., 2003).

2.1. Petrology of Santa María – Santiaguito

The chemical and petrological features of the Santa María – Santiaguito magmas have previously been described (Jicha et al., 2010; Rose, 1972, 1987; Scott et al., 2012, 2013; Singer et al., 2011, 2014), and we summarize the main points below. The Santa María magmas are typically basaltic andesite, but span a wide range of compositions from 51 wt% to 69 wt% SiO₂ (e.g. Rose, 1987). The earliest magmas erupted from Santiaguito itself were similar in composition to the 1902 pumice from Santa María (Rose 1972; Singer et al., 2011). Santiaguito eruptive products are typically porphyritic andesites to dacites (62–66 wt% SiO₂) with ~20–30 vol% plagioclase phenocrysts and ~5 vol% orthopyroxene + Fe-Ti oxides + augite ± olivine ± amphibole. The plagioclase phenocrysts commonly display one or more resorption surfaces with clear, euhedral rims; in many of the more recent samples the majority of the plagioclase crystals show severe resorption textures and a network of large, irregular, devitrified melt inclusions in the core. Accessory minerals include apatite, cristobalite, and pyrrhotite, the latter as inclusions in titanomagnetite phenocrysts. The groundmass consists of matrix glass, euhedral plagioclase, and equant to feathery microlites of orthopyroxene and titanomagnetite.

Glomerocrysts of plagioclase ± orthopyroxene ± olivine are common and contain large pools of interstitial glass (Fig. 1). These glomerocrysts preserve asymmetry at plagioclase-plagioclase-melt boundaries (Fig. 1d), due to the development of curved plagioclase-melt interfaces, rather than simple impingement textures with planar crystal surfaces. This suggests changes in the differential growth rates between different plagioclase crystallographic axes. These textures are similar to those observed in slowly cooling gabbroic cumulates (Holness et al., 2012) and, by analogy, suggests very slow growth. We therefore infer that these glomerocrysts may represent fragments of disrupted mush that would have gone on to form solid plutonic rocks at depth. Matrix and glomerocryst glass compositions range from ~66 to ~76 wt% SiO₂ and are similar to the compositions of melt inclusions (64.5–73.5 wt% SiO₂, Singer et al., 2014).

Thermobarometry based on amphibole phenocryst compositions suggests magma crystallisation temperatures of ~940–980 °C (±22 °C) at moderately oxidising conditions in the region of NNO + 0.5 to NNO + 2 (Scott et al., 2012; Singer et al., 2014), and this agrees with observed maximum surface eruption temperatures (850–950 °C, Sahetapy-Engel et al., 2004). Fe-Ti oxide compositions from the 1902 eruption give temperatures of 860–885 °C for the dacite and 925–1040 °C for the andesite (Singer et al., 2014). Petrological and geochemical studies of Santiaguito show that the lavas have become more mafic with time since the eruption recommenced in 1922 (Escobar Wolf et al., 2010; Scott et al., 2013).

Apatite is present in all samples as microphenocrysts and/or as inclusions within phenocryst phases (typically clinopyroxene), indicating early apatite saturation in the melt (Fig. 2). Some crystals are fully included within the host mineral while others are partly open to the matrix (Fig. 2), permitting variable degrees of equilibration with the host melt. The common occurrence of apatites included in pyroxene may be related to synneusis. The inclusions are equant and thus clearly distinct from the acicular quench crystals commonly observed in plagioclase phenocrysts elsewhere (e.g. Bacon, 1986; Wyllie et al., 1962), which are thought to form as a result of growth from a melt boundary

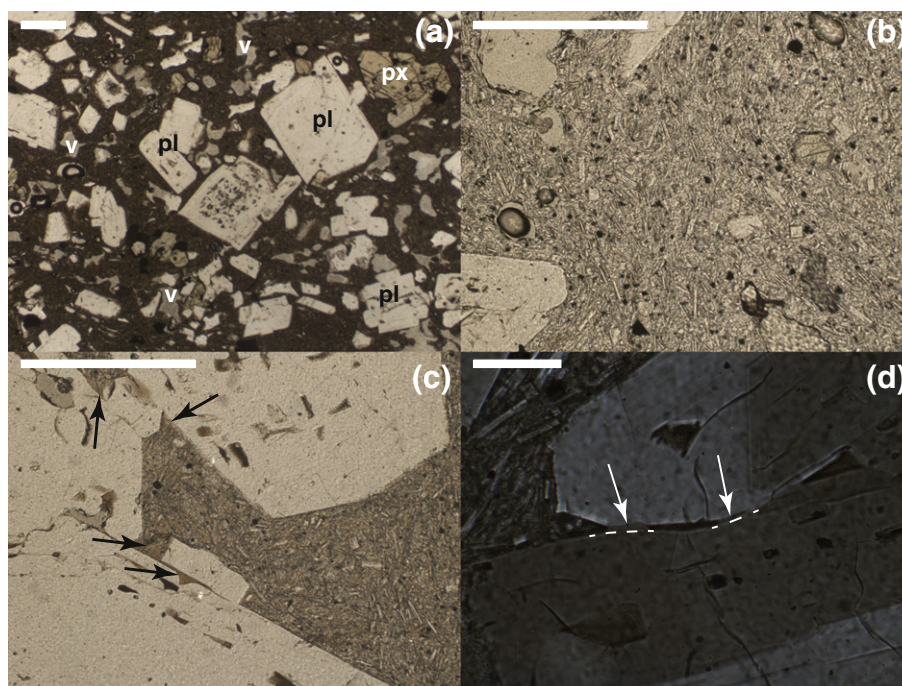


Fig. 1. Photomicrographs of typical dome rocks from Santiaguito Volcano. (a) Porphyritic texture with abundant plagioclase phenocrysts (pl), pyroxene (px) and vesicles (v). (b) Typical groundmass texture with abundant euhedral microlites of plagioclase, pyroxenes and oxides. (c) Matrix glass (arrowed) can be found as small patches and embayments near the margins of glomerocrysts. (d) Cumulate-type grain boundary textures are found in some plagioclase glomerocrysts. This is manifest as marked asymmetry of plagioclase-plagioclase junctions, resulting in small filaments of feldspar (arrowed; expected grain boundary marked with dashed line) joining adjacent grains of the glomerocryst. This is similar to that observed in gabbros (Holness et al., 2012) and suggests very slow cooling. Dark blebs are partially devitrified melt inclusions. Scale bar is 1 mm in all images except d (100 μ m).

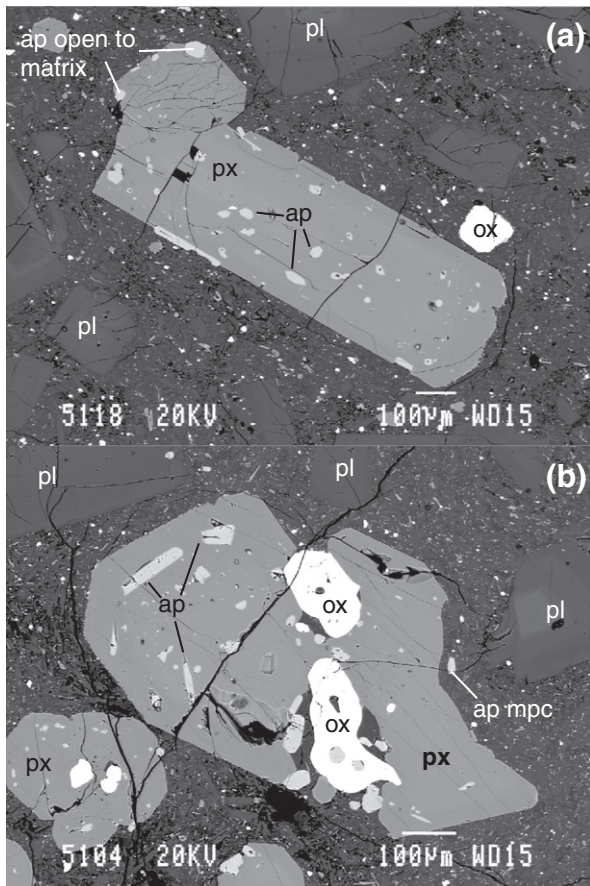


Fig. 2. Back-scattered electron SEM images showing typical occurrences of apatite in dome rocks from Santiaguito Volcano, both as abundant inclusions within pyroxene (px) phenocrysts or crystal clots of pyroxene with oxides (ox), and as microphenocrysts in the matrix. Some of the inclusions are open to the matrix (a). In (a) many of the apatite inclusions themselves contain tiny melt inclusions that appear as dark dots.

layer at the crystal-melt interface. Apatite microphenocrysts are texturally similar to those present as inclusions; their timing of crystallisation relative to the inclusions is unclear but we assume that the microphenocrysts were at least open to significant equilibration with the host melt. The apatites are relatively large, up to 150 µm in length, which is typically significantly larger than ground-mass plagioclase, orthopyroxene and titanomagnetite microlites.

2.2. Magma supply and fractionation

There is clear evidence of open-system processes at Santa-María – Santiaguito, with a large range of magma compositions erupted, from basaltic andesite to dacite. The deep supply of magma is dominated by hybrid basaltic andesites, fractionating amphibole in the deep crust and assimilating crustal material to form more silicic compositions (Jicha et al., 2010; Singer et al., 2011, 2014). The shallow magmatic system is thought to comprise an elongate, perhaps chemically stratified magma storage region (Rose, 1972; Scott et al., 2013), in which magmas decompress, degas and crystallise. There is clear evidence for mixing of more mafic magmas with the dacites (Singer et al., 2011, 2014) including reversely zoned plagioclase and the presence of mafic enclaves, as well as plutonic material.

2.3. Samples studied

Our dataset comes from analysis of 24 samples from Santiaguito, representing many of the dome and flow units of the complex, and dating from the 1920s to 2002, as reported in Scott et al. (2012,

supplementary table A) and in Scott (2012). We consider in detail the glass dataset of Scott et al. (2013, supplementary table D) together with some new glass analyses and a large dataset of apatite compositions.

3. Analytical methods

Mineral analyses were obtained by electron probe microanalysis on a four-spectrometer JEOL JXA-8600 electron microprobe in the Research Laboratory for Archaeology and the History of Art, University of Oxford. For apatite, long exposure to the electron beam results in sample damage in the form of volatile migration; this effect is strongly anisotropic and is most significant for halogen analyses conducted parallel to the c-axis of the crystal (e.g. Goldoff et al., 2012; Stock et al., 2015; Stormer et al., 1993). Selection of analytical beam conditions is a trade-off between the accuracy of halogen concentrations (needing a lower accelerating voltage and beam current to minimise electron beam-induced migration) and the precision of heavy and minor element analyses (e.g. Fe, Mn, requiring at least 15 kV accelerating voltage and higher beam currents, Stock et al., 2015). For most analyses, we used relatively short (30s) peak count times for all elements, a 15 kV accelerating voltage and a 15 nA defocused (5 µm) beam, with F, Cl and P analysed first. We found no discernible difference between analyses of grains with different crystallographic orientations, within the uncertainty of our analyses and the variance of the crystal population. We also analysed a subset of analyses using a 10 nA, 5 µm electron beam and these were consistent with the lower-F compositions of those analysed at 15 nA, albeit with slightly larger analytical uncertainties (see Table 1). For these analyses, 120 s peak counting times were used for F, Cl and S. Analyses with totals <95 wt% were excluded, as were those that did not give good stoichiometric formulae. Wilberforce and Durango apatite, oriented both parallel and perpendicular to the electron beam, were used as secondary standards to check the accuracy of the analyses. These did show slightly higher F contents for crystals oriented with the c-axis parallel to the electron beam, as demonstrated previously (e.g. Stormer et al., 1993). The sulphur peak position was checked prior to analysis and S was calibrated using BaSO₄. Analytical precision was typically better than 0.2 wt% for F, 0.13 wt% for Cl and ~500 ppm for S, and is given in Table 1.

We also performed element mapping on eighteen apatites from five different samples, including microphenocrysts and inclusions in pyroxene, using a JEOL JXA-8800 electron microprobe at the University of Oxford with a 15 kV, 15 nA electron beam. These crystals did not subsequently undergo quantitative analysis. Mapping used WDS for S, Cl, and F, and simultaneous EDS for all other elements (Al, Ca, Fe, K, Na, P, Si, Ti). Resulting images were 256 by 256 pixels, with a count time of ~45 microseconds per pixel.

For glasses, we used the existing matrix glass dataset of Scott et al. (2013) (see Table 2). We also analysed a small set of interstitial glasses from the glomerocrysts, using a 15 kV, 6 nA defocused (10 µm) beam, with alkalis analysed first to avoid electron-beam damage (e.g. Devine et al., 1995; Humphreys et al., 2006a). Peak counting times were 90s for F and S, 60s for Cl, 80s for Mg, 12 s for Na and 30s for all other elements. The sulphur peak position was checked prior to analysis and calibrated using BaSO₄.

4. Results

4.1. Apatite compositions

Apatites from Santiaguito are typically fluorapatite with ~0.6–1.5 wt% Cl (Table 1). Minor elements include ~0.2–1.2 wt% FeO, 0.1–0.35 wt% MgO, 0.1–0.5 wt% MnO, up to ~0.7 wt% SiO₂, and up to ~4000 ppm sulphur. There are no significant compositional differences between apatites in andesitic samples and those in the dacites, or between different phases of the eruption. The volatile contents of the

Table 1

Electron microprobe analyses of apatite. Analyses were taken in the centre of each 2D grain section unless otherwise specified.

Point identifier	Sample number		Analytical setup	Unit	Vent	Sample type	SiO ₂	FeO	MnO	MgO	CaO	P ₂ O ₅	SO ₃
12	SG-09-32	Inclusion	15 nA, 30s on peak	RmB	Monje	Dome	0.17	0.70		0.13	54.32	40.97	0.40
23	SG-09-32	Inclusion	15 nA, 30s on peak	RmB	Monje	Dome	0.14	0.61		0.20	53.52	41.11	0.22
32	SG-09-32	Inclusion	15 nA, 30s on peak	RmB	Monje	Dome	0.24	0.56		0.21	53.53	40.61	0.56
65	2006-69	Inclusion	15 nA, 30s on peak	-	Caliente	Bomb	0.13	0.45		0.24	53.67	39.50	0.44
70	2006-69	Inclusion	15 nA, 30s on peak	-	Caliente	Bomb	0.20	0.74		0.23	53.86	40.99	0.33
81	2006-69	Inclusion	15 nA, 30s on peak	-	Caliente	Bomb	0.16	0.75		0.25	53.32	39.57	0.45
83	2006-69	Inclusion	15 nA, 30s on peak	-	Caliente	Bomb	0.10	0.57		0.22	53.70	41.58	0.18
84	2006-69	Inclusion	15 nA, 30s on peak	-	Caliente	Bomb	0.09	0.47		0.24	54.14	39.33	0.22
100	SG-09-24	Inclusion	15 nA, 30s on peak	-	Caliente	Collapse	0.18	0.66		0.22	53.02	40.84	0.53
102	SG-09-24	Inclusion	15 nA, 30s on peak	-	Caliente	Collapse	0.13	0.89		0.24	53.36	40.96	0.29
103	SG-09-24	Inclusion	15 nA, 30s on peak	-	Caliente	Collapse	0.14	0.49		0.21	53.32	40.36	0.37
104	SG-09-24	Inclusion	15 nA, 30s on peak	-	Caliente	Collapse	0.11	0.42		0.14	53.64	39.93	0.23
108	SG-09-24	Inclusion	15 nA, 30s on peak	-	Caliente	Collapse	0.29	0.21		0.20	53.61	40.32	0.53
109	SG-09-24	Inclusion	15 nA, 30s on peak	-	Caliente	Collapse	0.20	0.87		0.23	53.34	39.83	0.34
125	SG-09-24	Inclusion	15 nA, 30s on peak	-	Caliente	Collapse	0.27	0.81		0.22	53.15	40.11	0.62
127	SG-09-24	Inclusion	15 nA, 30s on peak	-	Caliente	Collapse	0.14	0.44		0.24	53.89	41.12	0.23
104	SG-09-01	Inclusion	15 nA, 30s on peak	RcM1	Caliente	Flow	0.24	0.94	0.15	0.29	53.84	39.32	0.45
117	SG-09-01	Inclusion	15 nA, 30s on peak	RcM1	Caliente	Flow	0.23	0.74	0.19	0.26	53.63	39.10	0.44
119	SG-09-01	Inclusion	15 nA, 30s on peak	RcM1	Caliente	Flow	0.25	1.04	0.24	0.28	53.27	39.54	0.42
136	SG-09-01	Inclusion	15 nA, 30s on peak	RcM1	Caliente	Flow	0.15	0.94	0.54	0.33	53.16	39.02	0.30
145	SG-09-07	Inclusion	15 nA, 30s on peak	RcM3	Caliente	Flow	0.33	0.45	0.19	0.30	54.00	39.30	0.66
168	SG-09-07	Inclusion	15 nA, 30s on peak	RcM3	Caliente	Flow	0.28	0.31	0.18	0.25	54.93	38.97	0.30
232	SG-09-04	Inclusion	15 nA, 30s on peak	RcL	Caliente	Flow	0.35	0.82	0.13	0.31	54.01	39.27	0.37
34172_a1_2	SG-09-05	Inclusion	10 nA, 120 s on peak	RcL	Caliente	Flow	0.18	0.55	0.24	0.16	52.93	40.26	0.55
34172_a1_3	SG-09-05	Inclusion (rim)	10 nA, 120 s on peak	RcL	Caliente	Flow	0.13	0.84	0.21	0.19	52.82	41.09	0.35
34172_a1_4	SG-09-05	Inclusion	10 nA, 120 s on peak	RcL	Caliente	Flow	0.32	1.18	0.38	0.24	52.19	41.07	0.44
34172_a1_5	SG-09-05	Inclusion	10 nA, 120 s on peak	RcL	Caliente	Flow	0.38	0.98	0.28	0.23	53.11	40.49	0.72
34172_a1_7	SG-09-05	Inclusion	10 nA, 120 s on peak	RcL	Caliente	Flow	0.28	0.95	0.19	0.18	52.59	40.93	0.54
34172_a1_9	SG-09-05	Inclusion	10 nA, 120 s on peak	RcL	Caliente	Flow	0.69	0.98	0.21	0.21	52.83	40.13	1.01
34172_a3_3	SG-09-05	Inclusion	10 nA, 120 s on peak	RcL	Caliente	Flow	0.21	0.87	0.20	0.16	53.80	41.42	0.28
34172_a3_7	SG-09-05	Inclusion	10 nA, 120 s on peak	RcL	Caliente	Flow	0.35	0.80	0.10	0.17	52.93	40.85	0.72
34172_a4_1	SG-09-05	Inclusion	10 nA, 120 s on peak	RcL	Caliente	Flow	0.28	0.39	0.18	0.14	52.86	39.97	0.50
133	1121-67	Inclusion	15 nA, 30s on peak	Rb	Brujo	Dome	0.23	0.69		0.24	53.59	39.66	0.62
134	1121-67	Inclusion	15 nA, 30s on peak	Rb	Brujo	Dome	0.22	0.60		0.26	53.23	38.49	0.37
137	1121-67	Inclusion	15 nA, 30s on peak	Rb	Brujo	Dome	0.27	0.78		0.22	53.32	40.57	0.74
138	1121-67	Inclusion	15 nA, 30s on peak	Rb	Brujo	Dome	0.10	0.64		0.23	54.20	40.84	0.31
139	1121-67	Inclusion	15 nA, 30s on peak	Rb	Brujo	Dome	0.22	0.62		0.20	53.06	40.34	0.43
140	1121-67	Inclusion	15 nA, 30s on peak	Rb	Brujo	Dome	0.21	0.73		0.23	54.25	39.75	0.64
144	1121-67	Inclusion	15 nA, 30s on peak	Rb	Brujo	Dome	0.22	0.64		0.21	53.49	40.80	0.46
147	1121-67	Inclusion	15 nA, 30s on peak	Rb	Brujo	Dome	0.10	0.75		0.23	54.10	40.77	0.29
148	1121-67	Inclusion	15 nA, 30s on peak	Rb	Brujo	Dome	0.16	0.92		0.27	53.42	41.09	0.23
129	550-67	Inclusion	15 nA, 30s on peak	RbC	Brujo	Flow	0.14	0.72	0.20	0.26	54.65	39.29	0.15
8	SG-09-30	Inclusion	15 nA, 30s on peak	RbC	Brujo	Flow	0.11	0.76	0.34	0.25	54.05	40.46	0.23
9	SG-09-30	Inclusion	15 nA, 30s on peak	RbC	Brujo	Flow	0.09	0.74	0.31	0.24	53.26	40.51	0.17
12	SG-09-30	Inclusion	15 nA, 30s on peak	RbC	Brujo	Flow	0.23	0.86	0.42	0.23	53.84	40.12	0.39
35	SG-09-30	Inclusion	15 nA, 30s on peak	RbC	Brujo	Flow	0.21	0.79	0.11	0.21	54.30	39.68	0.35
41	SG-09-30	Inclusion	15 nA, 30s on peak	RbC	Brujo	Flow	0.23	0.77	0.22	0.24	53.97	40.91	0.38
42	SG-09-30	Inclusion	15 nA, 30s on peak	RbC	Brujo	Flow	0.19	0.81	0.19	0.27	53.86	39.81	0.36
167	SG-09-38	Inclusion	15 nA, 30s on peak	ReA	Mitad	Flow	0.33	0.74	0.17	0.24	53.88	40.36	0.41
80	2003-69	Inclusion	15 nA, 30s on peak	Re	Mitad	Dome	0.10	0.57	0.22	0.26	54.35	39.70	0.22
6	2002-69	Inclusion	15 nA, 30s on peak	Re	Mitad	Dome	0.25	0.81		0.22	53.57	39.92	0.44
21	SG-09-36	Inclusion	15 nA, 30s on peak	ReA	Mitad	Flow	0.15	0.73	0.22	0.22	53.84	38.92	0.34
Mean							0.21	0.71	0.23	0.23	53.59	40.19	0.41
stdev							0.10	0.19	0.10	0.04	0.54	0.75	0.17
Median							0.21	0.74	0.20	0.23	53.60	40.29	0.38
Point identifier	Sample number			Unit	Vent	Type	SiO ₂	FeO	MnO	MgO	CaO	P ₂ O ₅	SO ₃
58	2006-69	Open to matrix	15 nA, 30s on peak	-	Caliente	Bomb	0.16	0.54		0.23	54.05	39.93	0.28
64	2006-69	Open to matrix	15 nA, 30s on peak	-	Caliente	Bomb	0.22	0.71		0.25	53.90	40.42	0.47
66	2006-69	Open to matrix	15 nA, 30s on peak	-	Caliente	Bomb	0.24	0.93		0.19	53.73	40.62	0.25
68	2006-69	Open to matrix	15 nA, 30s on peak	-	Caliente	Bomb	0.19	0.68		0.19	53.83	39.92	0.35
69	2006-69	Open to matrix	15 nA, 30s on peak	-	Caliente	Bomb	0.10	0.60		0.26	54.24	38.75	0.20
71	2006-69	Open to matrix	15 nA, 30s on peak	-	Caliente	Bomb	0.26	0.82		0.23	53.92	39.99	0.55
74	2006-69	Open to matrix	15 nA, 30s on peak	-	Caliente	Bomb	0.09	0.32		0.25	54.39	41.07	0.12
85	2006-69	Open to matrix	15 nA, 30s on peak	-	Caliente	Bomb	0.28	0.68		0.26	54.48	41.23	0.32
99	SG-09-24	Open to matrix	15 nA, 30s on peak	-	Caliente	Collapse	0.33	0.56		0.16	52.06	36.64	0.26
124	SG-09-24	Open to matrix	15 nA, 30s on peak	-	Caliente	Collapse	0.17	1.24		0.29	54.01	40.73	0.24
141	1121-67	Open to matrix	15 nA, 30s on peak	Rb	Brujo	Dome	0.18	0.66		0.23	54.16	40.23	0.43
145	1121-67	Open to matrix	15 nA, 30s on peak	Rb	Brujo	Dome	0.17	0.35		0.23	54.05	41.43	0.27
146	1121-67	Open to matrix	15 nA, 30s on peak	Rb	Brujo	Dome	0.25	0.73		0.19	53.63	40.51	0.48
150	1121-67	Open to matrix	15 nA, 30s on peak	Rb	Brujo	Dome	0.38	0.60		0.20	53.23	39.73	0.34
151	1121-67	Open to matrix	15 nA, 30s on peak	Rb	Brujo	Dome	0.28	0.82		0.22	52.95	40.47	0.45
155	1121-67	Open to matrix	15 nA, 30s on peak	Rb	Brujo	Dome	0.24	1.09		0.24	54.01	40.64	0.49
157	1121-67	Open to matrix	15 nA, 30s on peak	Rb	Brujo	Dome	0.20	0.73		0.26	53.91	40.77	0.48

F	Cl	Total	O = F,Cl	S ppm	stdev F (wt%)	stdev Cl (wt%)	stdev S (ppm)	Si	Fe	Ca	Mg	Mn	S	P	F	Cl	OH*
1.38	1.40	99.47	0.90	1592	0.16	0.14	544	0.03	0.10	10.07	0.03		0.05	6.00	0.75	0.41	0.834
1.88	1.00	98.68	1.02	899	0.19	0.12	408	0.02	0.09	9.95	0.05		0.03	6.04	1.03	0.29	0.673
1.32	1.05	98.08	0.79	2254	0.16	0.12	646	0.04	0.08	10.02	0.05		0.07	6.01	0.73	0.31	0.962
1.19	1.17	96.80	0.77	1752	0.15	0.13	569	0.02	0.07	10.24	0.06		0.06	5.96	0.67	0.35	0.975
2.52	1.01	99.87	1.29	1327	0.22	0.12	495	0.03	0.11	9.91	0.06		0.04	5.96	1.37	0.29	0.337
1.08	1.36	96.94	0.76	1808	0.14	0.14	577	0.03	0.11	10.17	0.07		0.06	5.96	0.61	0.41	0.984
1.34	1.07	98.76	0.81	714	0.16	0.12	363	0.02	0.08	9.97	0.06		0.02	6.10	0.74	0.31	0.949
1.31	1.06	96.85	0.79	887	0.16	0.12	404	0.02	0.07	10.36	0.06		0.03	5.94	0.74	0.32	0.939
1.22	1.31	97.98	0.81	2133	0.15	0.13	627	0.03	0.10	9.93	0.06		0.07	6.04	0.68	0.39	0.937
2.41	1.44	99.72	1.34	1165	0.21	0.14	464	0.02	0.13	9.85	0.06		0.04	5.97	1.32	0.42	0.263
1.16	1.32	97.37	0.79	1483	0.15	0.13	523	0.03	0.07	10.08	0.06		0.05	6.03	0.65	0.39	0.956
1.61	1.54	97.63	1.03	902	0.17	0.15	408	0.02	0.06	10.16	0.04		0.03	5.97	0.90	0.46	0.636
2.59	1.18	98.93	1.36	2122	0.22	0.13	626	0.05	0.03	9.95	0.05		0.07	5.91	1.42	0.35	0.234
1.45	1.40	97.67	0.93	1366	0.16	0.14	502	0.03	0.13	10.10	0.06		0.05	5.96	0.81	0.42	0.770
1.27	1.52	97.98	0.88	2483	0.15	0.14	677	0.05	0.12	10.00	0.06		0.08	5.96	0.70	0.45	0.845
1.69	1.28	99.03	1.00	924	0.18	0.13	413	0.02	0.06	10.01	0.06		0.03	6.03	0.93	0.38	0.699
1.82	0.96	98.01	0.98	1811	0.19	0.11	553	0.04	0.14	10.17	0.08	0.02	0.06	5.87	1.01	0.29	0.698
1.50	1.09	97.19	0.88	1775	0.17	0.12	547	0.04	0.11	10.22	0.07	0.03	0.06	5.89	0.84	0.33	0.828
1.42	1.02	97.49	0.83	1685	0.17	0.12	533	0.04	0.15	10.11	0.07	0.04	0.06	5.93	0.80	0.31	0.897
1.26	1.37	97.05	0.84	1183	0.16	0.13	445	0.03	0.14	10.19	0.09	0.08	0.04	5.91	0.71	0.41	0.874
1.41	1.09	97.72	0.84	2645	0.16	0.12	665	0.06	0.07	10.21	0.08	0.03	0.09	5.87	0.79	0.33	0.887
2.64	0.92	98.78	1.32	1203	0.22	0.11	447	0.05	0.05	10.32	0.07	0.03	0.04	5.78	1.47	0.27	0.263
1.50	1.04	97.79	0.87	1463	0.17	0.12	490	0.06	0.12	10.23	0.08	0.02	0.05	5.88	0.84	0.31	0.848
1.17	1.19	97.23	0.76	2188	0.21	0.17	708	0.03	0.08	10.01	0.04	0.04	0.07	6.02	0.65	0.36	0.989
1.27	1.15	98.06	0.80	1390	0.22	0.16	565	0.02	0.12	9.89	0.05	0.03	0.05	6.08	0.70	0.34	0.956
1.04	1.36	98.22	0.74	1774	0.20	0.18	638	0.06	0.17	9.76	0.06	0.06	0.06	6.07	0.57	0.40	1.025
1.22	1.19	98.60	0.78	2868	0.21	0.17	811	0.07	0.14	9.91	0.06	0.04	0.09	5.97	0.67	0.35	0.975
1.12	1.15	97.92	0.73	2153	0.20	0.16	703	0.05	0.14	9.85	0.05	0.03	0.07	6.06	0.62	0.34	1.041
1.20	1.23	98.50	0.78	4053	0.21	0.17	963	0.12	0.14	9.85	0.05	0.03	0.13	5.91	0.66	0.36	0.975
1.59	1.05	99.58	0.91	1140	0.24	0.16	512	0.04	0.13	9.93	0.04	0.03	0.04	6.04	0.87	0.31	0.826
1.25	1.17	98.33	0.79	2880	0.22	0.16	812	0.06	0.12	9.86	0.04	0.01	0.09	6.02	0.69	0.34	0.966
1.40	1.12	96.85	0.84	2012	0.23	0.16	678	0.05	0.06	10.03	0.04	0.03	0.07	5.99	0.79	0.34	0.877
1.20	1.27	97.50	0.79	2473	0.15	0.13	676	0.04	0.10	10.15	0.06		0.08	5.93	0.67	0.38	0.951
1.17	1.24	95.58	0.77	1475	0.15	0.13	521	0.04	0.09	10.33	0.07		0.05	5.90	0.67	0.38	0.948
1.33	1.33	98.55	0.86	2975	0.16	0.14	742	0.05	0.11	9.94	0.06		0.10	5.98	0.73	0.39	0.879
1.20	1.26	98.79	0.79	1251	0.15	0.13	481	0.02	0.09	10.11	0.06		0.04	6.02	0.66	0.37	0.964
1.30	1.24	97.41	0.83	1704	0.16	0.13	561	0.04	0.09	10.02	0.05		0.06	6.02	0.73	0.37	0.902
1.33	1.14	98.27	0.82	2558	0.16	0.13	687	0.04	0.11	10.20	0.06		0.08	5.91	0.74	0.34	0.922
1.20	1.15	98.16	0.76	1856	0.15	0.13	586	0.04	0.09	10.01	0.05		0.06	6.03	0.66	0.34	0.998
1.19	1.31	98.74	0.80	1159	0.15	0.13	463	0.02	0.11	10.11	0.06		0.04	6.02	0.66	0.39	0.958
1.05	1.25	98.39	0.72	911	0.14	0.13	410	0.03	0.13	9.99	0.07		0.03	6.07	0.58	0.37	1.051
2.77	0.84	99.02	1.36	604	0.22	0.10	312	0.02	0.11	10.25	0.07	0.03	0.02	5.82	1.53	0.25	0.219
1.26	1.26	98.72	0.82	912	0.16	0.13	396	0.02	0.11	10.13	0.07	0.05	0.03	5.99	0.70	0.37	0.928
1.23	1.24	97.79	0.80	678	0.16	0.13	342	0.02	0.11	10.05	0.06	0.05	0.02	6.04	0.69	0.37	0.946
1.24	1.35	98.69	0.83	1567	0.16	0.13	519	0.04	0.13	10.10	0.06	0.06	0.05	5.95	0.69	0.40	0.913
2.10	0.97	98.71	1.10	1392	0.20	0.11	488	0.04	0.12	10.18	0.05	0.02	0.05	5.88	1.16	0.29	0.550
1.29	1.13	99.13	0.80	1514	0.16	0.12	509	0.04	0.11	10.03	0.06	0.03	0.05	6.01	0.71	0.33	0.961
1.29	1.14	97.91	0.80	1451	0.16	0.12	498	0.03	0.12	10.18	0.07	0.03	0.05	5.95	0.72	0.34	0.942
2.25	1.15	99.54	1.21	1637	0.20	0.12	513	0.06	0.11	9.98	0.06	0.03	0.05	5.91	1.23	0.34	0.432
2.39	1.02	98.83	1.24	882	0.21	0.12	387	0.02	0.08	10.18	0.07	0.03	0.03	5.88	1.32	0.30	0.375
1.14	1.26	97.61	0.76	1750	0.15	0.13	572	0.04	0.12	10.14	0.06	0.00	0.06	5.97	0.64	0.38	0.986
1.64	0.99	97.05	0.91	1346	0.18	0.11	473	0.03	0.11	10.30	0.06	0.03	0.05	5.88	0.92	0.30	0.776
1.50	1.19			1656													
0.46	0.15			687													
1.31	1.18			1541													

F	Cl	Total	O = F,Cl	S ppm	stdev F (wt%)	stdev Cl (wt%)	stdev S (ppm)	Si	Fe	Ca	Mg	Mn	S	P	F	Cl	OH*
2.08	0.83	98.11	1.06	1135	0.20	0.11	458	0.03	0.08	10.16	0.06		0.04	5.93	1.16	0.25	0.597
1.44	1.03	98.44	0.84	1875	0.16	0.12	589	0.04	0.10	10.08	0.06		0.06	5.97	0.79	0.31	0.899
2.52	1.40	99.88	1.38	1013	0.22	0.14	433	0.04	0.13	9.92	0.05		0.03	5.93	1.38	0.41	0.215
2.61	1.07	98.84	1.34	1383	0.22	0.12	506	0.03	0.10	10.05	0.05		0.05	5.89	1.44	0.32	0.247
2.14	0.98	97.28	1.12	813	0.20	0.12	387	0.02	0.09	10.36	0.07		0.03	5.85	1.20	0.30	0.498
2.44	1.01	99.21	1.26	2187	0.21	0.12	635	0.04	0.12	10.02	0.06		0.07	5.87	1.34	0.30	0.362
1.70	0.96	98.89	0.93	465	0.18	0.11	293	0.01	0.05	10.12	0.06		0.02	6.04	0.94	0.28	0.782
2.23	0.92	100.39	1.15	1269	0.20	0.11	484	0.05	0.10	9.97	0.07		0.04	5.96	1.21	0.27	0.527
2.46	0.92	93.38	1.24	1022	0.21	0.11	433	0.06	0.09	10.36	0.04		0.04	5.76	1.45	0.29	0.263
2.80	0.92	100.40	1.39	943	0.23	0.11	417	0.03	0.18	9.92	0.07		0.03	5.91	1.52	0.27	0.215
2.01	1.00	98.91	1.07	1733	0.19	0.12	566	0.03	0.10	10.10	0.06		0.06	5.93	1.11	0.29	0.599
2.32	0.78	99.61	1.15	1087	0.21	0.10	449	0.03	0.05	9.94	0.06		0.03	6.02	1.26	0.23	0.515
1.34	1.09	98.22	0.81	1934	0.16	0.12	598	0.04	0.11	10.05	0.05		0.06	6.00	0.74	0.32	0.938
2.79	1.33	98.58	1.47	1353	0.23	0.14	500	0.07	0.09	9.95	0.05		0.04	5.87	1.54	0.39	0.067
1.38	1.03	97.59	0.81	1797	0.16	0.12	576	0.05	0.12	9.97	0.06		0.06	6.02	0.77	0.31	0.928
2.62	0.93	100.25	1.31	1948	0.22	0.11	600	0.04	0.16	9.92	0.06		0.06	5.90	1.42	0.27	0.307

159	1121-67	Open to matrix	15 nA, 30s on peak	Rb	Brujo	Dome	0.28	0.72		0.21	53.89	40.05	0.56	
161	1121-67	Open to matrix	15 nA, 30s on peak	Rb	Brujo	Dome	0.09	0.50		0.23	53.77	40.65	0.20	
13	2002-69	Open to matrix	15 nA, 30s on peak	Re	Mitad	Dome	0.22	0.53		0.23	53.64	40.19	0.38	
20	2002-69	Open to matrix	15 nA, 30s on peak	Re	Mitad	Dome	0.24	0.87		0.33	53.99	39.13	0.21	
169	SG-09-38	Open to matrix	15 nA, 30s on peak	ReA	Mitad	Flow	0.45	0.68	0.20	0.31	53.74	39.22	0.35	
194	SG-09-38	Open to matrix (rim)	15 nA, 30s on peak	ReA	Mitad	Flow	0.30	0.82	0.24	0.23	54.06	39.36	0.47	
13	SG-09-30	Open to matrix	15 nA, 30s on peak	RbC	Brujo	Flow	0.19	0.68	0.23	0.24	54.61	39.93	0.19	
14	SG-09-30	Open to matrix	15 nA, 30s on peak	RbC	Brujo	Flow	0.24	0.85	0.26	0.21	53.74	41.15	0.30	
20	SG-09-30	Open to matrix	15 nA, 30s on peak	RbC	Brujo	Flow	0.19	0.48	0.18	0.24	54.77	38.98	0.26	
32	SG-09-30	Open to matrix (rim)	15 nA, 30s on peak	RbC	Brujo	Flow	0.32	1.14	0.30	0.23	53.34	38.53	0.32	
50	SG-09-30	Open to matrix (rim)	15 nA, 30s on peak	RbC	Brujo	Flow	0.48	0.69	0.21	0.24	54.18	38.35	0.90	
53	SG-09-30	Open to matrix	15 nA, 30s on peak	RbC	Brujo	Flow	0.10	0.60	0.25	0.24	54.05	38.82	0.17	
76	2003-69	Open to matrix	15 nA, 30s on peak	Re	Mitad	Dome	0.19	0.73	0.26	0.34	53.77	39.34	0.41	
111	SG-09-01	Open to matrix	15 nA, 30s on peak	RcM1	Caliente	Flow	0.33	0.89	0.14	0.35	53.70	38.49	0.28	
113	SG-09-01	Open to matrix	15 nA, 30s on peak	RcM1	Caliente	Flow	0.20	0.68	0.14	0.28	54.13	39.90	0.48	
122	SG-09-01	Open to matrix	15 nA, 30s on peak	RcM1	Caliente	Flow	0.22	0.78	0.16	0.25	54.10	39.33	0.39	
175	SG-09-07	Open to matrix (rim)	15 nA, 30s on peak	RcM3	Caliente	Flow	0.08	0.57	0.13	0.24	54.71	38.58	0.09	
177	SG-09-07	Open to matrix	15 nA, 30s on peak	RcM3	Caliente	Flow	0.13	1.19	0.21	0.28	54.41	39.47	0.12	
180	SG-09-07	Open to matrix	15 nA, 30s on peak	RcM3	Caliente	Flow	0.24	0.99	0.15	0.22	53.99	38.68	0.40	
192	SG-09-04	Open to matrix	15 nA, 30s on peak	RcL	Caliente	Flow	0.20	0.64	0.19	0.28	54.06	38.96	0.38	
212	SG-09-04	Open to matrix	15 nA, 30s on peak	RcL	Caliente	Flow	0.18	0.62	0.15	0.26	54.42	40.32	0.20	
218	SG-09-04	Open to matrix	15 nA, 30s on peak	RcL	Caliente	Flow	0.12	0.55	0.14	0.27	53.67	39.09	0.42	
220	SG-09-04	Open to matrix (rim)	15 nA, 30s on peak	RcL	Caliente	Flow	0.14	0.62	0.11	0.26	54.03	38.69	0.22	
235	SG-09-04	Open to matrix	15 nA, 30s on peak	RcL	Caliente	Flow	0.21	0.64	0.17	0.29	53.53	40.31	0.44	
244	802-66	Open to matrix	15 nA, 30s on peak	RmA	Monje	Flow	0.14	0.43	0.17	0.22	53.94	38.95	0.24	
							Mean	0.22	0.71	0.19	0.25	53.92	39.70	0.34
							stdev	0.09	0.21	0.05	0.04	0.47	0.98	0.15
							Median	0.21	0.68	0.18	0.24	53.99	39.91	0.33
Point identifier	Sample number			Unit	Vent	Type	SiO ₂	FeO	MnO	MgO	CaO	P ₂ O ₅	SO ₃	
78	2006-69	Microphenocryst	15 nA, 30s on peak	-	Caliente	Bomb	0.13	0.47		0.23	53.98	40.44	0.27	
152	1121-67	Microphenocryst	15 nA, 30s on peak	Rb	Brujo	Dome	0.09	0.61		0.23	53.70	40.83	0.18	
153	1121-67	Microphenocryst	15 nA, 30s on peak	Rb	Brujo	Dome	0.15	0.62		0.21	53.85	40.26	0.26	
158	1121-67	Microphenocryst	15 nA, 30s on peak	Rb	Brujo	Dome	0.15	0.46		0.22	54.25	41.04	0.33	
3	2002-69	Microphenocryst	15 nA, 30s on peak	Re	Mitad	Dome	0.16	0.39		0.20	53.90	40.67	0.40	
4	2002-69	Microphenocryst	15 nA, 30s on peak	Re	Mitad	Dome	0.43	0.69		0.21	53.42	39.15	0.34	
9	2002-69	Microphenocryst	15 nA, 30s on peak	Re	Mitad	Dome	0.22	0.51		0.20	53.78	40.31	0.36	
14	2002-69	Microphenocryst	15 nA, 30s on peak	Re	Mitad	Dome	0.36	0.45		0.20	53.44	39.80	0.05	
22	2002-69	Microphenocryst	15 nA, 30s on peak	Re	Mitad	Dome	0.24	0.64		0.20	53.35	38.86	0.25	
24	SG-09-36	Microphenocryst	15 nA, 30s on peak	ReA	Mitad	Flow	0.13	0.44	0.13	0.27	54.17	38.95	0.28	
172	SG-09-38	Microphenocryst	15 nA, 30s on peak	ReA	Mitad	Flow	0.15	0.62	0.17	0.22	54.14	38.13	0.26	
10	SG-09-30	Microphenocryst	15 nA, 30s on peak	RbC	Brujo	Flow	0.13	0.59	0.20	0.23	54.30	40.09	0.12	
11	SG-09-30	Microphenocryst	15 nA, 30s on peak	RbC	Brujo	Flow	0.08	0.35	0.16	0.23	54.30	40.93	0.11	
65	2003-69	Microphenocryst	15 nA, 30s on peak	Re	Mitad	Dome	0.11	0.27	0.21	0.21	54.88	39.16	0.21	
128	SG-09-01	Microphenocryst	15 nA, 30s on peak	RcM1	Caliente	Flow	0.19	0.60	0.18	0.21	54.46	38.83	0.23	
160	SG-09-07	Microphenocryst	15 nA, 30s on peak	RcM3	Caliente	Flow	0.19	0.35	0.08	0.22	54.54	39.78	0.42	
161	SG-09-07	Microphenocryst	15 nA, 30s on peak	RcM3	Caliente	Flow	0.20	0.50	0.16	0.23	54.56	38.35	0.44	
162	SG-09-07	Microphenocryst	15 nA, 30s on peak	RcM3	Caliente	Flow	0.25	0.57	0.12	0.24	54.15	38.46	0.48	
163	SG-09-07	Microphenocryst	15 nA, 30s on peak	RcM3	Caliente	Flow	0.18	0.26	0.13	0.18	54.68	39.56	0.34	
165	SG-09-07	Microphenocryst	15 nA, 30s on peak	RcM3	Caliente	Flow	0.10	0.38	0.12	0.27	54.80	39.93	0.19	
166	SG-09-07	Microphenocryst	15 nA, 30s on peak	RcM3	Caliente	Flow	0.21	0.60	0.12	0.28	54.03	39.23	0.52	
195	SG-09-04	Microphenocryst	15 nA, 30s on peak	RcL	Caliente	Flow	0.18	0.45	0.13	0.26	54.17	39.40	0.27	
196	SG-09-04	Microphenocryst	15 nA, 30s on peak	RcL	Caliente	Flow	0.31	0.53	0.15	0.24	54.31	37.30	0.26	
197	SG-09-04	Microphenocryst	15 nA, 30s on peak	RcL	Caliente	Flow	0.17	0.43	0.16	0.29	54.08	38.55	0.30	
206	SG-09-04	Microphenocryst	15 nA, 30s on peak	RcL	Caliente	Flow	0.20	0.57	0.11	0.26	54.15	38.86	0.41	
229	SG-09-04	Microphenocryst	15 nA, 30s on peak	RcL	Caliente	Flow	0.15	0.58	0.19	0.27	54.13	38.55	0.21	
34172_a1_6	SG-09-05	Microphenocryst	10 nA, 120 s on peak	RcL	Caliente	Flow	0.17	0.76	0.11	0.18	53.11	41.32	0.61	
34172_a3_1	SG-09-05	Microphenocryst	10 nA, 120 s on peak	RcL	Caliente	Flow	0.18	0.62	0.19	0.15	53.58	41.69	0.33	
34183_ap1_1	SG-09-16	Microphenocryst (rim)	10 nA, 120 s on peak	-	Caliente	Lahar deposit	0.19	0.38	0.18	0.16	53.38	40.94	0.25	
34183_ap1_2	SG-09-16	Microphenocryst (core)	10 nA, 120 s on peak	-	Caliente	Lahar deposit	0.19	0.37	0.20	0.16	52.98	39.00	0.32	
34183_ap1_3	SG-09-16	Microphenocryst (rim)	10 nA, 120 s on peak	-	Caliente	Lahar deposit	0.24	0.36	0.12	0.18	53.08	40.34	0.50	
34183_ap10_1	SG-09-16	Microphenocryst (rim)	10 nA, 120 s on peak	-	Caliente	Lahar deposit	0.20	0.33	0.20	0.19	53.44	41.00	0.47	
34183_ap10_2	SG-09-16	Microphenocryst (rim)	10 nA, 120 s on peak	-	Caliente	Lahar deposit	0.41	0.64	0.19	0.16	53.15	40.50	0.72	
34183_ap3_1	SG-09-16	Microphenocryst	10 nA, 120 s on peak	-	Caliente	Lahar deposit	0.40	0.36	0.13	0.16	53.10	39.42	0.99	
34204_ap12_1	SG-09-38	Microphenocryst	10 nA, 120 s on peak	ReA	Mitad	Flow	0.09	0.42	0.18	0.16	54.11	42.23	0.35	
34204_ap1_1	SG-09-38	Microphenocryst	10 nA, 120 s on peak	ReA	Mitad	Flow	0.04	0.40	0.11	0.14	52.99	41.55	0.20	
34204_ap10_1	SG-09-38	Microphenocryst	10 nA, 120 s on peak	ReA	Mitad	Flow	0.17	0.55	0.19	0.14	53.54	41.18	0.40	
34204_ap3_1	SG-09-38	Microphenocryst (rim)	10 nA, 120 s on peak	ReA	Mitad	Flow	0.07	0.25	0.09	0.15	53.75	41.73	0.20	
34204_ap3_2	SG-09-38	Microphenocryst (rim)	10 nA, 120 s on peak	ReA	Mitad	Flow	0.06	0.72	0.12	0.14	53.83	40.87	0.12	
34204_ap4_1	SG-09-38	Microphenocryst (core)	10 nA, 120 s on peak	ReA	Mitad	Flow	0.27	0.87	0.13	0.19	52.35	40.31	1.01	
34204_ap4_2	SG-09-38	Microphenocryst (rim)	10 nA, 120 s on peak	ReA	Mitad	Flow	0.22	0.40	0.21	0.15	53.47	40.60	0.33	
							Mean	0.19	0.50	0.15	0.20	53.84	39.95	0.35
							stdev	0.09	0.14	0.04	0.04	0.56	1.14	0.20
							Median	0.18	0.47	0.16	0.21	53.90	40.09	0.32

1.88	1.00	99.22	1.02	1912	0.19	0.12	594	0.04	0.10	9.99	0.07	0.06	5.97	1.03	0.29	0.681	
2.18	0.96	98.85	1.13	2232	0.20	0.11	642	0.05	0.11	10.04	0.05	0.07	5.90	1.20	0.28	0.519	
1.20	1.08	97.70	0.75	786	0.15	0.12	381	0.02	0.07	10.13	0.06	0.03	6.05	0.66	0.32	1.013	
2.65	1.20	99.04	1.39	1518	0.22	0.13	533	0.04	0.08	9.97	0.06	0.05	5.90	1.46	0.35	0.191	
2.20	1.40	98.37	1.24	825	0.20	0.14	392	0.04	0.13	10.20	0.09	0.03	5.84	1.23	0.42	0.354	
2.49	1.01	98.45	1.28	1411	0.21	0.11	476	0.08	0.10	10.10	0.08	0.03	5.82	1.38	0.30	0.318	
2.79	0.97	99.25	1.39	1890	0.22	0.11	550	0.05	0.12	10.08	0.06	0.04	0.06	5.80	1.54	0.28	0.177
3.10	0.69	99.85	1.46	754	0.24	0.10	360	0.03	0.10	10.11	0.06	0.03	0.02	5.84	1.70	0.20	0.104
3.17	0.89	100.81	1.53	1206	0.25	0.11	455	0.04	0.12	9.80	0.05	0.04	0.04	5.93	1.70	0.26	0.039
3.01	0.64	98.76	1.41	1054	0.24	0.09	425	0.03	0.07	10.28	0.06	0.03	0.03	5.78	1.67	0.19	0.139
2.95	1.03	98.16	1.48	1297	0.24	0.12	471	0.06	0.17	10.10	0.06	0.04	0.04	5.76	1.65	0.31	0.041
2.77	0.89	98.72	1.37	3602	0.23	0.11	784	0.08	0.10	10.17	0.06	0.03	0.12	5.69	1.54	0.26	0.200
2.66	1.50	98.39	1.46	678	0.23	0.14	340	0.02	0.09	10.23	0.06	0.04	0.02	5.81	1.48	0.45	0.067
2.58	1.33	98.94	1.39	1641	0.22	0.13	527	0.03	0.11	10.07	0.09	0.04	0.05	5.82	1.43	0.39	0.178
2.43	0.89	97.48	1.22	1109	0.22	0.11	432	0.06	0.13	10.23	0.09	0.02	0.04	5.79	1.36	0.27	0.368
1.69	0.99	98.49	0.93	1938	0.18	0.11	572	0.04	0.10	10.15	0.07	0.02	0.06	5.91	0.94	0.29	0.772
2.04	0.93	98.19	1.07	1556	0.20	0.11	512	0.04	0.11	10.21	0.06	0.02	0.05	5.86	1.14	0.28	0.584
2.74	0.74	97.89	1.32	375	0.23	0.10	249	0.01	0.08	10.40	0.06	0.02	0.01	5.79	1.54	0.22	0.240
2.13	0.81	98.75	1.08	475	0.20	0.10	281	0.02	0.18	10.24	0.07	0.03	0.02	5.87	1.19	0.24	0.574
2.31	0.99	97.98	1.20	1594	0.21	0.11	514	0.04	0.15	10.24	0.06	0.02	0.05	5.80	1.29	0.30	0.408
1.58	1.03	97.33	0.90	1517	0.17	0.12	501	0.04	0.10	10.31	0.07	0.03	0.05	5.87	0.89	0.31	0.800
2.80	1.15	100.12	1.44	809	0.23	0.12	365	0.03	0.09	10.05	0.07	0.02	0.03	5.88	1.53	0.34	0.138
1.58	1.10	96.95	0.91	1695	0.17	0.12	528	0.02	0.08	10.25	0.07	0.02	0.06	5.90	0.89	0.33	0.776
1.79	0.98	96.84	0.97	866	0.18	0.11	377	0.03	0.09	10.36	0.07	0.02	0.03	5.87	1.01	0.30	0.691
1.55	1.05	98.19	0.89	1747	0.17	0.12	536	0.04	0.09	10.04	0.08	0.02	0.06	5.97	0.86	0.31	0.830
1.25	1.11	96.44	0.78	958	0.15	0.12	396	0.02	0.06	10.38	0.06	0.03	0.03	5.92	0.71	0.34	0.953
2.25	1.01			1367													
0.54	0.18			602													
2.31	0.99			1325													
F	Cl	Total	O = F,Cl	S ppm	stdev F (wt%)	stdev Cl (wt%)	stdev S (ppm)	Si	Fe	Ca	Mg	Mn	S	P	F	Cl	OH*
2.21	0.98	98.71	1.15	1097	0.20	0.12	450	0.02	0.07	10.07	0.06		0.04	5.96	1.22	0.29	0.496
2.67	1.02	99.35	1.36	733	0.22	0.12	368	0.02	0.09	9.94	0.06		0.02	5.97	1.46	0.30	0.241
2.34	0.86	98.56	1.18	1061	0.21	0.11	442	0.03	0.09	10.06	0.06		0.03	5.94	1.29	0.25	0.453
2.75	0.81	100.01	1.34	1306	0.23	0.11	491	0.03	0.07	9.96	0.06		0.04	5.95	1.49	0.23	0.275
1.83	1.05	98.60	1.01	1616	0.19	0.12	550	0.03	0.06	10.05	0.05		0.05	5.99	1.01	0.31	0.686
1.70	0.96	96.88	0.93	1352	0.18	0.12	503	0.08	0.10	10.19	0.06		0.05	5.90	0.96	0.29	0.756
1.85	1.00	98.23	1.01	1447	0.19	0.12	520	0.04	0.07	10.08	0.05		0.05	5.97	1.02	0.30	0.678
1.57	1.10	96.95	0.91	207	0.17	0.12	197	0.06	0.07	10.17	0.05		0.01	5.98	0.88	0.33	0.788
1.67	1.16	96.38	0.96	1010	0.18	0.13	434	0.04	0.10	10.26	0.05		0.03	5.90	0.95	0.35	0.700
2.46	0.91	97.73	1.24	1133	0.22	0.11	434	0.02	0.06	10.27	0.07	0.02	0.04	5.84	1.37	0.27	0.353
2.68	0.86	97.23	1.32	1037	0.22	0.10	408	0.03	0.09	10.36	0.06	0.03	0.03	5.77	1.52	0.26	0.224
2.39	0.81	98.87	1.19	500	0.22	0.10	293	0.02	0.09	10.15	0.06	0.03	0.02	5.92	1.32	0.24	0.441
2.81	1.16	100.13	1.44	447	0.23	0.12	277	0.01	0.05	9.99	0.06	0.02	0.01	5.95	1.52	0.34	0.138
2.35	1.07	98.47	1.23	850	0.21	0.12	380	0.02	0.04	10.35	0.06	0.03	0.03	5.84	1.31	0.32	0.375
2.89	0.70	98.30	1.38	926	0.23	0.10	394	0.03	0.09	10.28	0.06	0.03	0.03	5.79	1.61	0.21	0.180
2.54	1.06	99.18	1.31	1662	0.22	0.12	526	0.03	0.05	10.16	0.06	0.01	0.05	5.85	1.40	0.31	0.289
2.36	0.78	97.58	1.17	1768	0.21	0.10	542	0.04	0.07	10.39	0.06	0.02	0.06	5.77	1.33	0.23	0.440
2.09	1.01	97.37	1.11	1920	0.20	0.11	565	0.04	0.09	10.33	0.06	0.02	0.06	5.79	1.18	0.31	0.517
2.19	1.15	98.65	1.18	1345	0.20	0.12	473	0.03	0.04	10.26	0.05	0.02	0.04	5.87	1.21	0.34	0.447
1.81	1.01	98.61	0.99	747	0.19	0.11	352	0.02	0.06	10.29	0.07	0.02	0.02	5.92	1.01	0.30	0.694
1.86	1.01	97.86	1.01	2072	0.19	0.11	587	0.04	0.09	10.22	0.07	0.02	0.07	5.86	1.04	0.30	0.662
1.69	1.00	97.55	0.94	1085	0.18	0.11	423	0.03	0.07	10.28	0.07	0.02	0.04	5.91	0.95	0.30	0.753
2.64	0.91	96.64	1.32	1059	0.22	0.11	417	0.06	0.08	10.49	0.07	0.02	0.04	5.69	1.50	0.28	0.217
1.81	0.98	96.77	0.98	1217	0.18	0.11	448	0.03	0.06	10.38	0.08	0.02	0.04	5.84	1.02	0.30	0.679
1.78	1.07	97.42	0.99	1630	0.18	0.12	518	0.04	0.09	10.31	0.07	0.02	0.05	5.85	1.00	0.32	0.678
1.71	0.94	96.74	0.93	843	0.18	0.11	372	0.03	0.09	10.41	0.07	0.03	0.03	5.86	0.97	0.29	0.741
1.42	1.16	98.83	0.86	2452	0.23	0.16	750	0.03	0.11	9.84	0.05	0.02	0.08	6.05	0.78	0.34	0.885
1.46	1.09	99.30	0.86	1335	0.23	0.16	553	0.03	0.09	9.89	0.04	0.03	0.04	6.08	0.80	0.32	0.885
2.03	0.85	98.33	1.04	981	0.28	0.14	475	0.03	0.05	9.95	0.04	0.03	0.03	6.03	1.12	0.25	0.634
1.57	1.03	95.82	0.89	1264	0.24	0.15	537	0.03	0.06	10.22	0.04	0.03	0.04	5.94	0.90	0.31	0.791
1.55	1.01	97.37	0.88	2004	0.24	0.15	676	0.04	0.05	10.00	0.05	0.02	0.07	6.01	0.86	0.30	0.838
1.38	1.06	98.27	0.82	1873	0.23	0.16	654	0.04	0.05	9.97	0.05	0.03	0.06	6.05	0.76	0.31	0.928
1.71	1.02	98.50	0.95	2884	0.25	0.15	811	0.07	0.09	9.90	0.04	0.03	0.09	5.96	0.94	0.30	0.762
1.61	1.08	97.24	0.92	3947	0.24	0.16	947	0.07	0.05	10.03	0.04	0.02	0.13	5.88	0.90	0.32	0.780
1.36	1.04	99.93	0.81	1392	0.23	0.16	566	0.02	0.06	9.91	0.04	0.03	0.04	6.11	0.74	0.30	0.963
1.34	1.08	97.85	0.81	793	0.22	0.16	426	0.01	0.06	9.91	0.04	0.02	0.03	6.14	0.74	0.32	0.939
2.06	1.06	99.30	1.11	1613	0.28	0.16	606	0.03	0.08	9.89	0.04	0.03	0.05	6.01	1.12	0.31	0.566
1.92	1.08	99.23	1.05	808	0.27	0.16	430	0.01	0.04	9.92	0.04	0.01	0.03	6.08	1.04	0.32	0.639
1.92	1.09	98.87	1.05	476	0.27	0.16	330	0.01	0.10	10.03	0.04	0.02	0.02	6.02	1.06	0.32	0.623
1.38	1.17	97.68	0.85	4039	0.23	0.16	959	0.05	0.13	9.82	0.05	0.02	0.13	5.97	0.76	0.35	0.889
1.99	0.83	98.19	1.03	1316	0.27	0.14	548	0.04	0.06	10.00	0.04	0.03	0.04	6.00	1.10	0.25	0.654
1.98	1.00			1396													
0.45	0.11			804													
1.86	1.02			1264													

Santiaguito apatites are similar to those of some other subduction-related systems for which data are available (Fig. 3). Apatite sulphur contents are similar in all textural associations. Those fully included in their host phenocrysts contain on average 1656 ppm S (1σ 687 ppm; $n = 52$), while those that are open to the matrix contain 1367 ppm S (1σ 602 ppm, $n = 42$) and microphenocrysts contain 1396 ppm S (1σ 804 ppm; $n = 41$; Table 1). In other words, the mean S concentrations from the population of apatites in each textural category are separated by less than one standard deviation. However, the data suggest that there are detectable differences in halogen concentrations for apatite in different textural situations (Table 1; see also Supplementary Figure), with the mean values of each apatite category separated by more than 1 standard deviation. Microphenocrysts record higher mean fluorine contents (1.98 wt% F, 1σ 0.45 wt%) and lower mean chlorine (1.00 wt% Cl, 1σ 0.11 wt%) than inclusions within phenocrysts (1.50 wt% F, 1σ 0.46 wt% and 1.19 wt% Cl, 1σ 0.15 wt%). Median concentrations are slightly lower for the microphenocrysts and inclusions (Table 1), reflecting a spread of a minority of data points to high F contents. Inclusions that are partially open to the matrix tend to record slightly higher mean F (2.25 wt%, 1σ 0.54 wt%) but similar mean Cl (1.01 wt%, 1σ 0.18 wt%) to the microphenocrysts. The rims of individual microphenocrysts systematically record lower Cl and higher F than the cores. We estimated OH contents for apatite using stoichiometry and assuming a fully occupied Z site (e.g. Piccoli and Candela, 2002); average calculated OH contents are 0.82 pfu for the apatite inclusions, compared with 0.46 pfu for inclusions open to the matrix and 0.60 pfu for the microphenocrysts (see Table 1). However, propagated OH uncertainties are very high and the assumption of complete stoichiometry may be unrealistic, particularly if significant C is present (e.g. Suetsugu et al., 2000).

Element mapping of individual crystals confirms that S, F, and Cl zoning is common even in very small apatites, but demonstrates that the form of the zoning may be quite variable. Apatites containing melt inclusions, or those entrapped adjacent to melt inclusions in the host phenocryst, commonly have patches enriched in F and Cl adjacent to the melt; S contents tend to be unaffected (Fig. 4a). Included apatites may contain sulphur-rich cores but typically do not show significant zoning of halogens. Inclusions open to the matrix also typically contain sulphur-rich cores and may show enrichment in fluorine towards the matrix, but with no equivalent systematic pattern in Cl contents (Fig. 4). Microphenocrysts may have sulphur-rich cores, and typically show F-rich rims (Fig. 4). Some grains show more complex sulphur zoning (Fig. 4).

4.2. Matrix glass compositions

The glass analyses presented include matrix glass, glass embayments at the margins of phenocrysts and glass trapped within glomerocrysts. The supplementary data from Scott et al. (2013) are given together with the new data in Table 2. Matrix glasses show a continuous range from 66–80 wt% SiO₂ and follow systematic major element variations. All the glasses show decreasing CaO, Na₂O and Al₂O₃ and increasing K₂O with increasing SiO₂. The MgO, CaO, FeO and TiO₂ contents of the matrix glasses decrease systematically with increasing bulk rock SiO₂ content, and the least evolved matrix glasses become more Si-rich (Fig. 5). The glasses plot along a systematic trend in the haplogranite ternary, and this has been interpreted as reflecting decompression crystallisation (Scott et al., 2012, fig. 11).

Glasses from most individual samples show a clear increase of K₂O and TiO₂ with increasing SiO₂, with glasses from the most evolved bulk rocks falling to lower concentrations at > 75 wt% SiO₂, but the overall picture is scattered (Fig. 5). A similar overall pattern is seen for FeO although the degree of scatter is higher and the downturn to lower FeO contents occurs at lower SiO₂. FeO does not correlate with K₂O or Al₂O₃, but correlates well with MgO (Fig. 5). The matrix glass compositions generally compare well with those of plagioclase-hosted melt inclusions from the 1902 dacite pumice and basaltic andesite scoria

(Singer et al., 2014; Fig. 5). The glomerocryst interstitial glasses are similar to the matrix glass, but with slightly lower CaO, slightly higher K₂O and TiO₂, and markedly higher FeO (Fig. 5).

Analytical totals are high in all the glasses analysed (Table 2), which suggests low dissolved H₂O concentrations. The matrix glasses contain up to 2400 ppm Cl, but the majority have much lower concentrations (average 835 ppm, 1σ 352 ppm, Table 2; Fig. 6). Overall, variations of Cl with SiO₂ show a similar pattern to TiO₂, with concentrations increasing with fractionation and then dropping towards lower Cl contents in the most evolved glasses (Fig. 6). F concentrations were consistently below detection limits (\sim 0.35 wt% F). Only a few glasses had sulphur contents above detection limit (\sim 135 ppm S); these contained 0.05–0.13 wt% SO₃ (200–520 ppm S). The interstitial glasses from the glomerocrysts typically contain higher Cl concentrations (1780 ± 440 ppm Cl, Fig. 6) but similar sulphur concentrations to the matrix glasses.

These data are more or less consistent with previously reported glass compositions in samples erupted from Santa María–Santiaguito, with the exception of apparently low H₂O contents in our samples, inferred from the lack of significantly low analytical totals. Villemant et al. (2003) reported bulk groundmass compositions for dome rocks with 0.07–0.93 wt% H₂O and 114–676 ppm Cl, whereas the bulk groundmass of Plinian fall deposits contained typically 1–1.5 wt% H₂O and 780–950 ppm Cl. Volatile contents of matrix glass in clasts from the 1902 Plinian eruption were 0.55–2.4 wt% H₂O (estimated by difference) and 937–1397 ppm Cl (Villemant et al., 2003). Balcone-Boissard et al. (2010) reported similar halogen contents, also for melt inclusions from Plinian clasts from the 1902–1929 eruptions (100–300 ppm F, 700–1600 ppm Cl), but with much higher H₂O contents (estimated at 5–7 wt% H₂O). Singer et al. (2014) analysed H₂O in plagioclase-hosted melt inclusions from the 1902 dacite pumice by secondary ion mass spectrometry and recorded concentrations up to 6.85 wt% H₂O.

5. Discussion

5.1. Interpretation of glass compositional variations

Taken together, the matrix glass compositions exhibit chemical trends that indicate progressive fractionation driven by decompression and degassing; this is consistent with the progressive decrease in H₂O content seen in plagioclase-hosted melt inclusions (Singer et al., 2014). The increase in MgO, FeO, TiO₂ and K₂O with SiO₂ in individual samples suggests that fractionation is dominated by plagioclase \pm pyroxene, consistent with the observed modal abundance of \sim 75–80% plagioclase within the phenocryst assemblage (Scott et al., 2013). The most silica-rich glasses can only have formed at very low pressures, and the wide range of normative SiO₂ contents seen in the whole dataset is consistent with crystallisation of hydrous magma over a wide pressure range (Blundy and Cashman, 2001). The presence of amphibole phenocrysts in some of the more evolved rocks indicates crystallisation at \sim 150 MPa or more (assuming H₂O saturation; e.g. Browne and Gardner, 2006). Phase equilibria experiments (Andrews, 2014) suggest that the Santa Maria 1902 dacite was stored at pressures similar to 150–170 MPa (if H₂O-saturated) at 850 °C prior to eruption. Face-value application of the thermobarometer proposed by Ridolfi et al. (2010) indicates crystallisation depths > 12 km (Scott et al., 2013), and there is also geochemical evidence of substantial fractionation of amphibole from the magma, seen as a decrease in Dy/Yb with increasing SiO₂ and La/Lu in the whole-rock dataset of Scott et al. (2013). Although pressures predicted by the Ridolfi et al. (2010) barometer are likely to be over-estimated (Andrews, 2014; Erdmann et al., 2014), these data together indicate polybaric crystallisation in the Santa María – Santiaguito system. The interpretation of decompression crystallisation is supported by the well-developed groundmass and amphibole breakdown textures (Scott et al., 2012); the high H₂O contents of melt inclusions (Singer et al., 2014) and successful phase equilibria

Table 2
Electron microprobe analyses of glasses.

Point identifier	Sample number	Vent	Bulk rock SiO ₂ wt%	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Cl	Total	stdev Cl wt%	S ppm	Cl ppm	Reference		
1	SG-09-01	Caliente	61.99	76.23	0.62	10.76	2.87		0.98	0.95	3.51	3.86	0.31	bd	0.142	100.24	0.074		1424	Matrix glass	Scott et al. (2013) supplementary data	
2	SG-09-01	Caliente	61.99	69.87	0.42	17.48	1.29		0.23	3.35	5.76	2.10	0.05	bd	0.046	100.59	0.042		455	Matrix glass	Scott et al. (2013) supplementary data	
3	SG-09-01	Caliente	61.99	67.74	0.23	18.06	1.76		0.63	3.89	5.93	1.67	0.09	bd	0.046	100.04	0.042		464	Matrix glass	Scott et al. (2013) supplementary data	
5	SG-09-01	Caliente	61.99	73.04	0.47	13.00	2.14		0.78	1.59	4.80	2.97	0.16	bd	0.063	99.02	0.049		629	Matrix glass	Scott et al. (2013) supplementary data	
6	SG-09-01	Caliente	61.99	72.59	0.45	15.44	1.03		0.08	2.24	5.46	2.60	0.06	bd	0.051	100.00	0.045		514	Matrix glass	Scott et al. (2013) supplementary data	
7	SG-09-01	Caliente	61.99	70.53	0.43	16.46	1.14		0.24	3.00	5.41	2.42	0.12	bd	0.062	99.81	0.049		619	Matrix glass	Scott et al. (2013) supplementary data	
10	SG-09-01	Caliente	61.99	67.38	0.41	17.82	2.03		0.43	3.54	5.98	1.62	0.09	bd	bd	99.30					Matrix glass	Scott et al. (2013) supplementary data
11	SG-09-01	Caliente	61.99	69.54	0.44	16.68	2.18		0.44	3.53	5.32	2.34	0.20	bd	bd	100.67					Matrix glass	Scott et al. (2013) supplementary data
13	SG-09-01	Caliente	61.99	74.00	0.40	14.06	1.51		0.29	1.84	4.92	2.95	0.18	bd	0.047	m	0.042		465	Matrix glass	Scott et al. (2013) supplementary data	
14	SG-09-01	Caliente	61.99	71.46	0.35	16.27	0.96		0.11	2.60	5.85	1.98	0.04	bd	0.060	99.69	0.048		601	Matrix glass	Scott et al. (2013) supplementary data	
15	SG-09-01	Caliente	61.99	74.87	0.60	12.09	2.68		0.76	1.29	4.39	3.32	0.20	bd	0.069	100.27	0.052		687	Matrix glass	Scott et al. (2013) supplementary data	
16	SG-09-01	Caliente	61.99	75.17	0.66	12.30	2.44		0.49	1.05	4.49	3.39	0.13	bd	0.085	100.22	0.057		852	Matrix glass	Scott et al. (2013) supplementary data	
17	SG-09-01	Caliente	61.99	71.26	0.44	15.34	1.99		0.39	2.42	5.13	2.62	0.16	bd	0.062	99.82	0.049		618	Matrix glass	Scott et al. (2013) supplementary data	
18	SG-09-01	Caliente	61.99	77.91	0.57	11.58	1.38		0.18	0.43	4.05	3.92	0.08	bd	0.094	100.19	0.060		941	Matrix glass	Scott et al. (2013) supplementary data	
19	SG-09-07	Caliente	62.38	70.75	0.44	14.37	1.94		0.45	2.24	5.14	3.38	0.31	bd	0.078	99.09	0.055		781	Matrix glass	Scott et al. (2013) supplementary data	
21	SG-09-07	Caliente	62.38	68.87	0.57	16.70	2.23		0.09	3.52	6.15	1.47	0.09	bd	bd	99.69					Matrix glass	Scott et al. (2013) supplementary data
23	SG-09-07	Caliente	62.38	75.34	0.44	13.04	1.28		0.12	0.91	4.42	4.46	0.09	bd	0.141	100.25	0.074		1411	Matrix glass	Scott et al. (2013) supplementary data	
25	SG-09-07	Caliente	62.38	68.86	0.36	16.39	2.00		0.54	3.46	5.18	2.87	0.32	bd	0.076	100.04	0.054		761	Matrix glass	Scott et al. (2013) supplementary data	
26	SG-09-07	Caliente	62.38	74.82	0.60	11.47	2.25		0.56	0.94	3.81	4.36	0.17	bd	0.132	99.11	0.071		1316	Matrix glass	Scott et al. (2013) supplementary data	
27	SG-09-07	Caliente	62.38	71.73	0.35	15.73	1.35		0.38	2.81	5.36	2.46	0.28	bd	0.047	100.49	0.043		474	Matrix glass	Scott et al. (2013) supplementary data	
51	SG-09-05	Caliente	62.52	68.53	0.30	17.99	1.37		0.25	3.65	6.01	1.99	0.15	bd	bd	100.25					Matrix glass	Scott et al. (2013) supplementary data
52	SG-09-05	Caliente	62.52	72.37	0.44	14.96	1.76		0.30	2.10	5.72	2.54	0.08	bd	0.067	100.34	0.051		673	Matrix glass	Scott et al. (2013) supplementary data	
53	SG-09-05	Caliente	62.52	76.78	0.69	11.49	2.22		0.35	0.65	4.19	3.61	0.13	bd	0.103	100.21	0.063		1030	Matrix glass	Scott et al. (2013) supplementary data	
54	SG-09-05	Caliente	62.52	76.43	0.63	12.11	2.18		0.31	0.86	4.48	3.59	0.10	bd	0.096	100.79	0.061		962	Matrix glass	Scott et al. (2013) supplementary data	
58	SG-09-05	Caliente	62.52	70.59	0.42	15.85	1.90		0.61	3.01	5.15	2.49	0.17	bd	0.041	100.25	0.040		412	Matrix glass	Scott et al. (2013) supplementary data	
59	SG-09-05	Caliente	62.52	75.50	0.57	11.77	2.34		0.61	0.98	4.21	3.45	0.26	bd	0.078	99.77	0.055		779	Matrix glass	Scott et al. (2013) supplementary data	
60	SG-09-05	Caliente	62.52	70.44	0.45	16.62	1.62		0.23	3.14	5.59	2.37	0.10	bd	0.067	100.63	0.051		671	Matrix glass	Scott et al. (2013) supplementary data	
61	SG-09-05	Caliente	62.52	76.18	0.62	12.63	1.80		0.08	0.86	4.70	3.36	0.10	bd	0.084	100.42	0.057		836	Matrix glass	Scott et al. (2013) supplementary data	
62	SG-09-05	Caliente	62.52	76.28	0.61	12.33	1.47		0.08	0.72	4.67	3.54	0.13	bd	0.078	99.90	0.055		780	Matrix glass	Scott et al. (2013) supplementary data	
63	SG-09-05	Caliente	62.52	72.24	0.44	15.80	1.32		0.12	2.50	5.73	2.56	0.11	bd	0.052	100.85	0.045		518	Matrix glass	Scott et al. (2013) supplementary data	
64	SG-09-05	Caliente	62.52	71.64	0.47	15.27	1.59		0.27	2.58	5.55	2.59	0.19	bd	0.052	100.19	0.045		518	Matrix glass	Scott et al. (2013) supplementary data	
66	SG-09-05	Caliente	62.52	75.05	0.59	12.86	1.56		0.07	1.11	4.56	3.43	0.07	bd	0.088	99.39	0.058		875	Matrix glass	Scott et al. (2013) supplementary data	
67	SG-09-05	Caliente	62.52	72.67	0.41	15.04	1.45		0.06	2.05	5.40	2.68	0.05	bd	0.075	99.88	0.054		749	Matrix glass	Scott et al. (2013) supplementary data	
69	SG-09-05	Caliente	62.52	67.46	0.30	18.40	1.21		0.09	4.19	5.87	1.85	0.10	bd	0.050	99.51	0.044		496	Matrix glass	Scott et al. (2013) supplementary data	
70	SG-09-04	Caliente	62.56	71.62	0.33	16.35	1.22		0.08	2.63	5.76	2.32	0.11	bd	0.060	100.49	0.048		604	Matrix glass	Scott et al. (2013) supplementary data	
71	SG-09-04	Caliente	62.56	76.34	0.52	12.66	1.86		0.31	1.03	4.47	3.18	0.11	bd	0.073	100.54	0.053		731	Matrix glass	Scott et al. (2013) supplementary data	
72	SG-09-04	Caliente	62.56	73.82	0.52	13.57	1.60		0.25	1.51	4.87	3.07	0.20	bd	0.087	99.49	0.058		873	Matrix glass	Scott et al. (2013) supplementary data	
73	SG-09-04	Caliente	62.56	77.71	0.59	11.88	1.79		0.04	0.50	4.30	3.78	0.06	bd	0.108	100.75	0.064		1075	Matrix glass	Scott et al. (2013) supplementary data	
75	SG-09-04	Caliente	62.56	77.69	0.58	11.81	1.76		0.13	0.55	4.27	3.77	0.14	0.076	0.092	100.87	0.060	304	922	Matrix glass	Scott et al. (2013) supplementary data	
76	SG-09-04	Caliente	62.56	68.82	0.31	17.85	1.27		0.13	3.63	5.93	2.05	0.07	bd	0.041	100.10	0.040		411	Matrix glass	Scott et al. (2013) supplementary data	
77	SG-09-04	Caliente	62.56	67.44	0.34	18.45	1.41		0.26	4.25	5.78	1.68	0.26	bd	0.067	99.94	0.051		670	Matrix glass	Scott et al. (2013) supplementary data	
78	SG-09-04	Caliente	62.56	69.85	0.38	16.98	1.33		0.25	3.01	6.01	2.12	0.07	bd	bd	100.01					Matrix glass	Scott et al. (2013) supplementary data
79	SG-09-04	Caliente	62.56	76.12	0.53	12.69	1.48		0.07	0.89	4.63	3.58	0.10	bd	bd	100.09					Matrix glass	Scott et al. (2013) supplementary data
80	SG-09-04	Caliente	62.56	70.18	0.32	16.99	1.43		0.18	3.12	5.90	2.08	0.11	bd	bd	100.30					Matrix glass	Scott et al. (2013) supplementary data
81	SG-09-04	Caliente	62.56	76.52	0.54	12.64	1.57		0.04	0.78	4.63	3.54	0.10	bd	0.084	100.45	0.057		837	Matrix glass	Scott et al. (2013) supplementary data	
82	SG-09-04	Caliente	62.56	75.28	0.58	13.15	1.51		0.06	1.28	4.51	3.41	0.15	bd	0.086	100.01	0.057		856	Matrix glass	Scott et al. (2013) supplementary data	
83	SG-09-04	Caliente	62.56	77.69	0.56	12.10	1.59		0.08	0.54	4.38	3.69	0.10	bd	0.081	100.82	0.056		808	Matrix glass	Scott et al. (2013) supplementary data	
84	SG-09-04	Caliente	62.56	77.99	0.60	11.91	1.39		0.06	0.43	4.31	3.77	0.13	bd	0.071	100.67	0.052		711	Matrix glass	Scott et al. (2013) supplementary data	
88	SG-09-03	Caliente	62.41	72.02	0.50	15.07	1.37		0.16	2.24	5.16	2.81	0.13	bd	0.063	99.51	0.049		631	Matrix glass	Scott et al. (2013) supplementary data	
89	SG-09-03	Caliente	62.41	74.39	0.66	11.86	2.76		0.69	0.95	4.04	3.59	0.17	bd	0.077	99.18	0.054		773	Matrix glass	Scott et al. (2013) supplementary data	
90	SG-09-03	Caliente	62.41	70.90	0.47	15.97	0.92		0.12	2.74	5.40	2.64	0.09	bd	0.057	99.31	0.047		573	Matrix glass	Scott et al. (2013) supplementary data	
91	SG-09-03	Caliente	62.41	72.73	0.44	13.90	2.05		0.62	1.88	5.41	1.88	0.12	bd	bd	99.02					Matrix glass	Scott et al. (2013) supplementary data
92	SG-09-03	Caliente	62.41	74.84	0.62	12.18	1.74		0.36	0.95	4.18	3.75	0.21	bd	0.129	98.96	0.070		1290	Matrix glass	Scott et al. (2013) supplementary data	
93	SG-09-03	Caliente	62.41	66.08	0.27	18.09	2.25		1.01	4.19	5.76	1.64	0.22	bd	0.040	99.53	0.039		400	Matrix glass	Scott et al. (2013) supplementary data	

(continued on next page)

Table 2 (continued)

Point identifier	Sample number	Vent	Bulk rock SiO ₂ wt%	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Cl	Total	stdev Cl wt%	S ppm	Cl ppm	Reference	
94	SG-09-03	Caliente	62.41	67.27	0.30	18.67	1.24		0.28	3.79	6.07	1.71	0.12	bd	bd	99.45			Matrix glass	Scott et al. (2013) supplementary data	
95	SG-09-03	Caliente	62.41	76.57	0.64	11.15	1.73		0.19	0.39	3.77	4.21	0.11	bd	0.160	98.92	0.078	1597	Matrix glass	Scott et al. (2013) supplementary data	
97	SG-09-03	Caliente	62.41	75.18	0.51	13.76	0.90		0.06	1.26	4.88	3.43	0.10	bd	0.054	100.13	0.045	536	Matrix glass	Scott et al. (2013) supplementary data	
98	SG-09-03	Caliente	62.41	71.69	0.44	15.85	1.17		0.17	2.51	5.10	2.87	0.08	bd	0.082	99.96	0.056	820	Matrix glass	Scott et al. (2013) supplementary data	
99	SG-09-03	Caliente	62.41	77.08	0.57	12.05	1.10		0.11	0.62	4.33	4.01	0.11	bd	0.075	100.06	0.053	746	Matrix glass	Scott et al. (2013) supplementary data	
100	SG-09-03	Caliente	62.41	76.96	0.66	11.48	2.10		0.22	0.61	3.83	4.07	0.27	bd	0.085	100.29	0.057	849	Matrix glass	Scott et al. (2013) supplementary data	
102	SG-09-03	Caliente	62.41	71.37	0.42	16.08	1.19		0.12	2.64	5.41	2.59	0.05	bd	0.087	99.95	0.057	867	Matrix glass	Scott et al. (2013) supplementary data	
103	SG-09-03	Caliente	62.41	68.67	0.42	16.96	2.12		0.44	4.04	5.04	2.30	0.10	bd	0.062	100.16	0.048	617	Matrix glass	Scott et al. (2013) supplementary data	
2	SG-09-09	Lahar	62.76	74.05	0.70	11.50	3.16		0.74	0.94	4.25	3.66	0.20	bd	0.160	99.38	0.076	1595	Matrix glass	Scott et al. (2013) supplementary data	
7	SG-09-09	Lahar	62.76	74.56	0.70	11.98	2.43		0.22	0.52	4.39	4.40	0.05	0.078	0.239	99.57	0.087	314	2393	Matrix glass	Scott et al. (2013) supplementary data
8	SG-09-09	Lahar	62.76	73.54	0.66	12.38	2.42		0.28	0.93	5.69	2.57	0.08	bd	0.159	98.69	0.071	1589	Matrix glass	Scott et al. (2013) supplementary data	
11	1234-67	-	-	67.89	0.21	17.83	1.15		0.25	3.51	5.67	1.98	0.06	bd	0.064	98.61	0.045	644	Matrix glass	Scott et al. (2013) supplementary data	
12	1234-67	-	-	78.16	0.41	11.68	1.12		0.18	0.68	4.13	3.57	0.11	bd	0.116	100.15	0.061	1160	Matrix glass	Scott et al. (2013) supplementary data	
13	1234-67	-	-	73.89	0.23	15.15	1.18		0.31	2.03	5.41	2.39	0.14	bd	0.070	100.80	0.047	701	Matrix glass	Scott et al. (2013) supplementary data	
14	1234-67	-	-	68.84	0.19	18.61	1.14		0.28	3.36	6.74	1.56	0.06	bd	bd	100.77			Matrix glass	Scott et al. (2013) supplementary data	
15	1234-67	-	-	72.69	0.27	14.77	1.26		0.36	1.78	5.20	2.57	0.05	bd	0.069	99.01	0.048	686	Matrix glass	Scott et al. (2013) supplementary data	
16	1234-67	-	-	75.75	0.40	13.39	1.47		0.13	1.36	4.60	3.09	0.13	bd	0.068	100.39	0.051	681	Matrix glass	Scott et al. (2013) supplementary data	
35	SG-09-06	Caliente	63.08	68.84	0.25	18.17	1.47		0.29	3.73	6.13	1.74	0.07	bd	bd	100.69			Matrix glass	Scott et al. (2013) supplementary data	
37	SG-09-06	Caliente	63.08	77.43	0.55	11.38	1.51		0.23	0.60	4.06	4.16	0.19	bd	0.106	100.21	0.064	1062	Matrix glass	Scott et al. (2013) supplementary data	
38	SG-09-06	Caliente	63.08	76.81	0.45	12.26	1.62		0.35	0.92	4.26	3.70	0.14	bd	0.073	100.57	0.053	734	Matrix glass	Scott et al. (2013) supplementary data	
39	SG-09-06	Caliente	63.08	73.74	0.42	13.98	1.67		0.39	2.23	4.79	3.18	0.15	bd	0.077	100.62	0.055	771	Matrix glass	Scott et al. (2013) supplementary data	
40	SG-09-06	Caliente	63.08	76.69	0.50	12.08	1.72		0.14	0.77	4.29	3.69	0.16	bd	0.100	100.15	0.062	1003	Matrix glass	Scott et al. (2013) supplementary data	
41	SG-09-06	Caliente	63.08	68.24	0.29	17.61	1.21		0.34	3.91	5.81	1.87	0.11	bd	bd	99.38			Matrix glass	Scott et al. (2013) supplementary data	
42	SG-09-06	Caliente	63.08	72.20	0.35	14.67	2.14		0.58	2.32	5.36	2.71	0.20	bd	0.076	100.60	0.054	760	Matrix glass	Scott et al. (2013) supplementary data	
44	SG-09-06	Caliente	63.08	74.24	0.42	14.05	1.03		0.18	1.60	4.96	2.91	0.07	bd	0.067	99.52	0.051	666	Matrix glass	Scott et al. (2013) supplementary data	
45	SG-09-06	Caliente	63.08	70.21	0.37	16.31	1.81		0.63	3.01	5.46	2.37	0.16	bd	0.089	100.42	0.058	885	Matrix glass	Scott et al. (2013) supplementary data	
49	SG-09-06	Caliente	63.08	67.98	0.29	18.35	1.50		0.31	3.80	6.07	1.82	0.15	bd	0.058	100.33	0.047	577	Matrix glass	Scott et al. (2013) supplementary data	
18	SG-09-38	Mitad	63.28	75.15	0.33	13.65	1.52		0.08	1.35	5.09	3.12	0.02	bd	0.062	100.35	0.049	622	Matrix glass	Scott et al. (2013) supplementary data	
19	SG-09-38	Mitad	63.28	67.40	0.29	17.90	1.21		0.03	3.21	6.23	2.11	0.06	bd	0.028	98.48	0.033	281	Matrix glass	Scott et al. (2013) supplementary data	
21	SG-09-38	Mitad	63.28	74.94	0.37	14.10	1.30		0.22	1.70	5.01	2.86	0.12	bd	0.079	100.71	0.055	788	Matrix glass	Scott et al. (2013) supplementary data	
22	SG-09-38	Mitad	63.28	72.26	0.38	15.24	1.49		0.23	2.56	5.04	2.62	0.25	bd	0.076	100.13	0.054	757	Matrix glass	Scott et al. (2013) supplementary data	
23	SG-09-38	Mitad	63.28	74.73	0.41	13.55	1.70		0.32	1.45	4.60	3.05	0.08	bd	0.088	99.97	0.058	875	Matrix glass	Scott et al. (2013) supplementary data	
24	SG-09-23	Caliente	64.91	70.93	0.18	16.62	1.09		0.32	2.15	6.11	2.59	0.09	bd	0.029	100.09	0.034	291	Matrix glass	Scott et al. (2013) supplementary data	
29	SG-09-29	Brujo	63.78	72.40	0.28	15.67	1.03		0.05	2.15	4.73	3.44	0.07	bd	0.072	99.88	0.053	717	Matrix glass	Scott et al. (2013) supplementary data	
33	SG-09-29	Brujo	63.78	76.44	0.40	12.14	0.83		0.04	0.53	4.44	3.25	0.09	bd	0.090	98.25	0.059	896	Matrix glass	Scott et al. (2013) supplementary data	
1	SG-09-32	Monje	64.1	78.57	0.15	12.47	0.27		0.00	1.37	4.67	2.13	0.05	bd	bd	99.68			Matrix glass	Scott et al. (2013) supplementary data	
2	SG-09-32	Monje	64.1	79.99	0.33	10.77	0.89		0.25	0.33	3.51	3.41	0.04	bd	0.044	99.55	0.042	441	Matrix glass	Scott et al. (2013) supplementary data	
4	SG-09-32	Monje	64.1	77.44	0.21	11.67	0.58		0.09	0.87	4.09	3.05	0.08	bd	0.049	98.13	0.044	488	Matrix glass	Scott et al. (2013) supplementary data	
5	SG-09-32	Monje	64.1	73.19	0.50	14.07	1.34		0.23	0.41	3.75	5.12	0.04	bd	0.197	98.85	0.087	1974	Matrix glass	Scott et al. (2013) supplementary data	
6	SG-09-32	Monje	64.1	76.71	0.37	12.46	0.93		0.03	0.62	4.01	3.91	0.02	bd	0.097	99.15	0.061	971	Matrix glass	Scott et al. (2013) supplementary data	
8	SG-09-32	Monje	64.1	73.40	0.26	15.21	1.05		0.23	2.09	5.45	2.56	0.03	bd	0.091	100.36	0.059	912	Matrix glass	Scott et al. (2013) supplementary data	
9	SG-09-32	Monje	64.1	70.79	0.12	16.88	0.60		0.01	2.53	6.13	2.51	0.02	bd	bd	99.62			Matrix glass	Scott et al. (2013) supplementary data	

13	SG-09-32	Monje	64.1	77.45	0.17	12.93	0.36	0.00	0.66	4.88	3.56	0.03	bd	bd	100.04			Matrix glass	Scott et al. (2013) supplementary data	
14	SG-09-32	Monje	64.1	79.57	0.38	10.71	1.25	0.07	0.54	3.66	2.79	0.06	bd	bd	99.03			Matrix glass	Scott et al. (2013) supplementary data	
16	SG-09-32	Monje	64.1	73.70	0.14	14.47	0.69	0.09	1.58	5.47	2.76	0.08	bd	0.054	99.05	0.046	543	Matrix glass	Scott et al. (2013) supplementary data	
17	SG-09-32	Monje	64.1	77.98	0.20	12.10	0.41	0.00	0.85	4.68	3.03	0.04	bd	bd	99.30			Matrix glass	Scott et al. (2013) supplementary data	
18	SG-09-34	Monje	64.59	75.50	0.71	11.36	2.91	0.40	0.57	3.54	4.69	0.11	bd	0.174	99.97	0.082	1744	Matrix glass	Scott et al. (2013) supplementary data	
19	SG-09-34	Monje	64.59	70.99	0.28	17.00	0.90	0.11	2.45	6.03	2.39	0.07	bd	0.067	100.29	0.051	667	Matrix glass	Scott et al. (2013) supplementary data	
20	SG-09-34	Monje	64.59	75.73	0.32	13.76	1.06	0.12	1.28	4.75	3.31	0.10	bd	0.100	100.54	0.062	998	Matrix glass	Scott et al. (2013) supplementary data	
22	SG-09-34	Monje	64.59	70.52	0.27	16.72	1.13	0.17	2.69	5.39	2.96	0.08	bd	0.083	100.01	0.057	829	Matrix glass	Scott et al. (2013) supplementary data	
23	SG-09-34	Monje	64.59	74.85	0.30	13.57	1.84	0.55	1.42	5.06	2.80	0.05	bd	0.074	100.52	0.054	744	Matrix glass	Scott et al. (2013) supplementary data	
24	SG-09-34	Monje	64.59	69.96	0.23	17.41	1.07	0.17	2.81	6.15	2.39	0.07	0.082	0.069	100.41	0.052	327	694	Matrix glass	Scott et al. (2013) supplementary data
25	SG-09-34	Monje	64.59	76.33	0.43	11.81	1.63	0.49	0.87	4.17	4.00	0.19	bd	0.104	100.02	0.063	1042	Matrix glass	Scott et al. (2013) supplementary data	
26	SG-09-34	Monje	64.59	76.09	0.23	13.35	0.67	0.17	1.64	5.08	2.07	0.12	bd	0.040	99.46	0.039	398	Matrix glass	Scott et al. (2013) supplementary data	
28	SG-09-34	Monje	64.59	77.46	0.48	10.66	1.58	0.12	0.20	3.44	4.92	0.09	bd	0.107	99.06	0.064	1071	Matrix glass	Scott et al. (2013) supplementary data	
31	SG-09-34	Monje	64.59	76.79	0.38	12.48	1.12	0.33	1.44	4.17	2.68	0.33	bd	0.100	99.81	0.062	998	Matrix glass	Scott et al. (2013) supplementary data	
32	SG-09-34	Monje	64.59	70.03	0.25	16.98	0.78	0.16	2.53	6.05	1.75	0.08	bd	bd	98.60			Matrix glass	Scott et al. (2013) supplementary data	
33	SG-09-34	Monje	64.59	75.86	0.19	14.07	0.63	0.06	1.96	5.26	1.74	0.05	bd	bd	99.83			Matrix glass	Scott et al. (2013) supplementary data	
34	SG-09-34	Monje	64.59	72.29	0.42	14.28	1.94	0.51	1.73	4.46	3.80	0.18	bd	0.071	99.67	0.052	714	Matrix glass	Scott et al. (2013) supplementary data	
35	2006-69	Caliente	-	78.41	0.39	11.87	1.27	0.15	0.84	4.38	3.06	0.05	bd	0.076	100.49	0.054	757	Matrix glass	Scott et al. (2013) supplementary data	
36	2006-69	Caliente	-	68.63	0.24	18.19	0.99	0.15	3.76	5.87	1.92	0.05	bd	bd	99.79			Matrix glass	Scott et al. (2013) supplementary data	
37	2006-69	Caliente	-	73.38	0.22	14.25	1.51	0.55	1.63	5.73	2.37	0.04	bd	0.048	99.74	0.043	484	Matrix glass	Scott et al. (2013) supplementary data	
38	2006-69	Caliente	-	68.13	0.21	19.42	0.86	0.05	4.03	6.07	1.89	0.06	bd	0.042	100.75	0.040	424	Matrix glass	Scott et al. (2013) supplementary data	
39	2006-69	Caliente	-	76.76	0.47	11.19	1.96	0.29	0.60	3.70	3.99	0.27	bd	0.117	99.34	0.067	1169	Matrix glass	Scott et al. (2013) supplementary data	
41	2006-69	Caliente	-	77.00	0.42	12.76	1.04	0.07	1.13	4.52	3.05	0.06	bd	0.088	100.14	0.058	880	Matrix glass	Scott et al. (2013) supplementary data	
42	2006-69	Caliente	-	74.56	0.36	13.57	1.48	0.08	1.29	4.51	3.57	0.07	bd	0.084	99.57	0.057	837	Matrix glass	Scott et al. (2013) supplementary data	
43	2006-69	Caliente	-	70.99	0.29	16.34	1.33	0.07	2.40	5.75	2.57	0.09	bd	0.044	99.88	0.041	442	Matrix glass	Scott et al. (2013) supplementary data	
45	2006-69	Caliente	-	75.01	0.35	12.90	1.28	0.08	0.99	4.66	3.32	0.07	bd	0.106	98.77	0.064	1060	Matrix glass	Scott et al. (2013) supplementary data	
46	2006-69	Caliente	-	74.91	0.38	13.57	1.07	0.07	1.36	5.19	2.80	0.05	bd	0.050	99.45	0.044	501	Matrix glass	Scott et al. (2013) supplementary data	
47	2006-69	Caliente	-	69.82	0.19	17.39	1.11	0.23	3.44	5.74	1.62	0.11	bd	bd	99.65			Matrix glass	Scott et al. (2013) supplementary data	
48	2006-69	Caliente	-	78.91	0.41	10.71	1.57	0.07	0.35	3.70	3.77	0.05	bd	bd	99.54			Matrix glass	Scott et al. (2013) supplementary data	
49	2006-69	Caliente	-	77.73	0.44	11.70	1.32	0.10	0.61	4.44	3.40	0.07	bd	0.088	99.90	0.058	877	Matrix glass	Scott et al. (2013) supplementary data	
51	SG-09-24	Caliente	65.92	73.79	0.12	13.70	0.93	0.34	1.39	4.87	2.89	0.07	bd	0.056	98.18	0.046	558	Matrix glass	Scott et al. (2013) supplementary data	
53	SG-09-24	Caliente	65.92	77.12	0.31	11.08	1.76	0.68	0.91	3.82	3.07	0.16	0.082	0.136	99.13	0.072	327	1358	Matrix glass	Scott et al. (2013) supplementary data
54	SG-09-24	Caliente	65.92	77.91	0.21	12.30	0.63	0.16	1.04	4.46	2.79	0.00	bd	0.054	99.54	0.046	541	Matrix glass	Scott et al. (2013) supplementary data	
55	SG-09-24	Caliente	65.92	75.95	0.31	12.28	0.99	0.16	0.77	4.07	3.57	0.05	bd	0.115	98.27	0.066	1146	Matrix glass	Scott et al. (2013) supplementary data	
56	SG-09-24	Caliente	65.92	76.86	0.16	13.31	0.54	0.19	1.56	5.11	2.18	0.05	bd	bd	99.96			Matrix glass	Scott et al. (2013) supplementary data	
57	SG-09-24	Caliente	65.92	75.97	0.18	13.34	0.76	0.28	1.54	5.09	2.40	0.11	bd	bd	99.67			Matrix glass	Scott et al. (2013) supplementary data	
58	SG-09-24	Caliente	65.92	79.65	0.25	11.27	0.58	0.11	1.00	4.44	2.05	0.07	bd	bd	99.42			Matrix glass	Scott et al. (2013) supplementary data	
59	SG-09-24	Caliente	65.92	79.18	0.16	11.51	0.69	0.09	0.78	3.95	2.87	0.08	bd	0.050	99.35	0.044	502	Matrix glass	Scott et al. (2013) supplementary data	
60	SG-09-24	Caliente	65.92	75.56	0.21	13.04	0.71	0.15	1.15	4.68	2.99	0.08	bd	0.065	98.64	0.050	645	Matrix glass	Scott et al. (2013) supplementary data	
61	SG-09-24	Caliente	65.92	78.46	0.16	12.25	0.60	0.21	1.04	4.73	2.84	0.08	bd	bd	100.39			Matrix glass	Scott et al. (2013) supplementary data	
62	SG-09-24	Caliente	65.92	74.90	0.31	14.25	0.81	0.33	1.66	5.10	2.47	0.11	bd	bd	99.93			Matrix glass	Scott et al. (2013) supplementary data	
63	SG-09-24	Caliente	65.92	76.59	0.38	12.62	1.14	0.16	1.24	4.36	3.40	0.07	bd	0.135	100.09	0.072	1345	Matrix glass	Scott et al. (2013) supplementary data	
66	SG-09-24	Caliente	65.92	75.15	0.16	13.98	0.50	0.18	1.51	5.11	2.69	0.06	bd	bd	99.34			Matrix glass	Scott et al. (2013) supplementary data	
67	SG-09-24	Caliente	65.92	74.48	0.25	13.19	1.45	0.41	0.94	4.43	3.90	0.02	bd	0.117	99.16	0.067	1168	Matrix glass	Scott et al. (2013) supplementary data	
69	1000-67	Mitad	65.74	67.17	0.49	17.95	1.25	0.07	3.39	5.34	3.06	0.12	bd	0.164	99.00	0.079	1638	Matrix glass	Scott et al. (2013) supplementary data	

(continued on next page)

Table 2 (continued)

Point identifier	Sample number	Vent	Bulk rock SiO ₂ wt%	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Cl	Total	stdev Cl wt%	S ppm	Cl ppm		Reference
74	1000-67	Mitad	65.74	68.45	0.47	17.55	1.35		0.06	3.53	5.28	2.76	0.14	bd	0.114	99.71	0.066		1144	Matrix glass	Scott et al. (2013) supplementary data
83	1000-67	Mitad	65.74	66.57	0.46	18.61	1.15		0.08	4.01	5.64	2.58	0.14	bd	0.018	99.26	0.026		181	Matrix glass	Scott et al. (2013) supplementary data
84	1000-67	Mitad	65.74	69.65	0.58	16.58	1.50		0.04	2.44	5.47	3.62	0.21	bd	0.143	100.23	0.074		1427	Matrix glass	Scott et al. (2013) supplementary data
85	1121-67	Brujo	-	75.69	0.61	11.50	2.48		0.36	0.62	4.23	3.83	0.17	bd	0.087	99.57	0.058		870	Matrix glass	Scott et al. (2013) supplementary data
86	1121-67	Brujo	-	74.16	0.38	14.32	1.25		0.15	1.44	5.15	3.37	0.12	bd	0.088	100.43	0.058		879	Matrix glass	Scott et al. (2013) supplementary data
88	1121-67	Brujo	-	75.35	0.31	12.34	1.88		0.82	1.21	4.51	2.87	0.25	bd	0.086	99.62	0.057		860	Matrix glass	Scott et al. (2013) supplementary data
89	1121-67	Brujo	-	77.83	0.35	11.20	1.09		0.05	0.66	3.85	3.33	0.06	bd	0.075	98.50	0.053		747	Matrix glass	Scott et al. (2013) supplementary data
90	1121-67	Brujo	-	74.02	0.34	13.41	1.47		0.34	1.12	4.87	3.36	0.12	bd	0.071	99.13	0.052		707	Matrix glass	Scott et al. (2013) supplementary data
92	1121-67	Brujo	-	68.90	0.22	18.22	0.77		0.09	2.63	6.84	2.31	0.05	bd	0.049	100.09	0.043		486	Matrix glass	Scott et al. (2013) supplementary data
93	1121-67	Brujo	-	70.93	0.29	15.25	1.75		0.47	2.09	4.97	3.33	0.11	0.089	0.082	99.37	0.056	358	819	Matrix glass	Scott et al. (2013) supplementary data
94	1121-67	Brujo	-	75.06	0.38	12.06	1.92		0.36	0.77	3.92	4.43	0.25	bd	0.156	99.31	0.077		1563	Matrix glass	Scott et al. (2013) supplementary data
95	1121-67	Brujo	-	77.06	0.49	11.44	1.58		0.21	0.30	3.76	4.62	0.03	bd	0.120	99.60	0.068		1202	Matrix glass	Scott et al. (2013) supplementary data
97	1121-67	Brujo	-	78.14	0.40	11.63	1.31		0.09	0.71	4.11	3.41	0.07	bd	0.072	99.95	0.052		718	Matrix glass	Scott et al. (2013) supplementary data
98	1121-67	Brujo	-	73.18	0.35	14.61	0.98		0.05	1.41	5.23	3.60	0.01	bd	0.094	99.52	0.060		943	Matrix glass	Scott et al. (2013) supplementary data
99	1121-67	Brujo	-	78.99	0.29	10.87	0.91		0.13	0.83	4.02	2.60	0.07	bd	0.070	98.79	0.052		700	Matrix glass	Scott et al. (2013) supplementary data
100	1121-67	Brujo	-	72.85	0.34	14.74	1.30		0.14	1.65	4.84	3.24	0.06	bd	0.121	99.28	0.068		1210	Matrix glass	Scott et al. (2013) supplementary data
34172_m5_1	SG-09-05	Caliente	63.08	73.59	0.51	14.66	1.53	0.05	0.09	1.65	5.27	3.08	0.15	bd	bd	100.60				Matrix glass	New data (this study)
34172_m7_2	SG-09-05	Caliente	63.08	74.47	0.60	13.53	2.16	0.01	0.16	0.77	4.66	3.88	0.16	bd	0.129	100.53	0.076		1285	Glomerocryst glass	New data (this study)
34172_m4_2	SG-09-05	Caliente	63.08	74.71	0.67	12.91	2.45	0.08	0.21	0.80	4.64	3.87	0.20	bd	0.226	100.75	0.101		2257	Glomerocryst glass	New data (this study)
34172_m7_1	SG-09-05	Caliente	63.08	74.20	0.72	13.29	2.52	0.07	0.16	0.80	4.87	3.76	0.19	bd	0.147	100.73	0.081		1465	Glomerocryst glass	New data (this study)
34172_m6_1	SG-09-05	Caliente	63.08	73.62	0.71	13.45	2.62	0.05	0.14	0.74	4.79	3.82	0.21	bd	0.222	100.37	0.100		2222	Glomerocryst glass	New data (this study)
34172_mg3_3	SG-09-05	Caliente	63.08	73.22	0.58	13.30	2.72	0.13	0.21	1.17	6.23	2.05	0.18	bd	0.170	99.98	0.088		1703	Glomerocryst glass	New data (this study)
34172_m6_3	SG-09-05	Caliente	63.08	75.03	0.71	12.16	2.75	0.16	0.37	0.84	4.32	3.59	0.20	bd	0.120	100.24	0.074		1203	Glomerocryst glass	New data (this study)
34172_mg4_1	SG-09-05	Caliente	63.08	71.87	0.61	14.80	2.89	0.16	0.20	1.45	6.41	1.95	0.19	bd	0.169	100.69	0.088		1693	Glomerocryst glass	New data (this study)
34172_m6_2	SG-09-05	Caliente	63.08	73.21	0.73	13.22	3.01	0.04	0.19	0.97	4.69	3.79	0.22	bd	0.244	100.32	0.105		2439	Glomerocryst glass	New data (this study)
34172_mg1_1	SG-09-05	Caliente	63.08	72.34	0.62	13.69	3.22	0.10	0.26	1.46	6.96	1.04	0.23	bd	0.219	100.14	0.100		2188	Glomerocryst glass	New data (this study)
34172_m3_4	SG-09-05	Caliente	63.08	73.69	0.82	11.12	4.29	0.18	0.83	1.59	4.24	3.33	0.28	0.068	0.180	100.61	0.090	274	1800	Glomerocryst glass	New data (this study)
34172_m3_3	SG-09-05	Caliente	63.08	71.02	0.82	12.30	4.52	0.03	0.78	2.17	4.57	3.66	0.26	bd	0.187	100.32	0.092		1866	Glomerocryst glass	New data (this study)
34183_mg1_3	SG-09-16	Caliente	-	69.42	0.39	17.20	1.79	0.07	0.33	3.53	5.37	2.13	0.14	bd	bd	100.37				Glomerocryst glass	New data (this study)
34183_mg1_2	SG-09-16	Caliente	-	75.96	0.62	12.25	2.17	0.05	0.11	0.67	4.58	3.92	0.11	bd	0.106	100.54	0.069		1059	Glomerocryst glass	New data (this study)
34183_mg4_1	SG-09-16	Caliente	-	72.40	0.58	14.11	2.51	0.08	0.20	0.91	5.39	3.84	0.18	bd	0.146	100.33	0.081		1463	Glomerocryst glass	New data (this study)
34183_mg3_2	SG-09-16	Caliente	-	73.54	0.64	12.63	2.57	0.05	0.21	0.95	4.68	3.50	0.19	bd	0.149	99.13	0.082		1488	Glomerocryst glass	New data (this study)
34183_mg4_2	SG-09-16	Caliente	-	71.94	0.63	13.77	3.05	0.16	0.34	1.12	5.02	3.63	0.21	0.048	0.192	100.12	0.093	191	1921	Glomerocryst glass	New data (this study)
34183_mg4_3	SG-09-16	Caliente	-	71.36	0.63	13.67	3.62	0.16	0.43	1.13	5.04	3.70	0.19	bd	0.244	100.18	0.105		2438	Glomerocryst glass	New data (this study)

experiments (Andrews, 2014); and positive correlations between FeO, TiO₂ and MgO, and CaO and Al₂O₃ in the glasses, suggesting crystallisation of pyroxene, Fe-Ti oxides and plagioclase.

The high FeO and TiO₂ contents of the glomerocryst glass embayments may support the interpretation that some of the erupted crystal load is derived from disaggregated plutonic material that represents the fractionation products of the magma, perhaps prior to saturation of Fe-Ti oxides. The glomerocryst and matrix glasses have very low H₂O contents compared with melt inclusion compositions reported in previous studies (c.f. Balcone-Boissard et al., 2010). We interpret this as variable diffusional loss of H₂O during magma ascent, degassing and crystallisation. However, the glomerocryst glasses retain high Cl and F concentrations, probably due to much slower (minimal) diffusion of halogens from these crystal clots during ascent. Overall, the glomerocryst glass compositions suggest that they represent partially re-equilibrated fragments of early-formed crystal mush.

5.2. Behaviour of the halogens

With SiO₂ or K₂O as an index of differentiation, Cl contents of the glasses increase during fractionation from ~0.03 wt% to >0.15 wt% Cl, then decrease after ~75 wt% SiO₂. This indicates incompatible behaviour of Cl until the later stages of crystallisation, when it undergoes exsolution into a fluid phase, consistent with the conclusions of Villemant et al. (2003) based on correlation between H₂O and Cl contents of glass. Fluorine concentrations of the glasses were below detection limits. However, we can use the volatile contents of apatite to give more information on the evolution of volatiles during magma ascent and crystallisation.

The F/Cl ratio of apatite is dependent on the ratio of halogen fugacities, $f_{\text{HF}}/f_{\text{HCl}}$, as well as temperature and pressure (Piccoli and Candela, 1994). Therefore, in the absence of additional information, the cause of the observed compositional change is difficult to determine without ambiguity. The observation of higher F and lower Cl contents in the apatite microphenocrysts relative to inclusions could be produced by decreasing temperature, or by increasing pressure (Doherty et al., 2014; Piccoli and Candela, 2002). Recent work also indicates that Cl partitioning between apatite and melt in the presence of a fluid phase is dependent primarily on melt halogen (Cl) concentration, with a subsidiary dependence on pressure (Cl concentrations in apatite increasing with decreasing pressure; Doherty et al., 2014; Webster et al., 2009). We cannot rule out that decreasing temperature during crystallisation played a role in the changing apatite compositions. However, a number of factors suggest that the changing apatite chemistry is related to compositional variations in the coexisting melt and/or fluid. Firstly, the correlation between H₂O and Cl in glasses (Villemant et al., 2003), indicates that the magma reached fluid saturation and exsolution resulted in decreasing Cl concentrations in the melt. Loss of Cl from the melt by exsolution of a fluid phase, together with incompatible, non-volatile behaviour of F (i.e. F does not migrate into the free fluid phase but increases in concentration in the melt) would be consistent with increasing $f_{\text{HF}}/f_{\text{HCl}}$ during crystallisation and degassing. This would require loss of Cl to occur between crystallisation of the pyroxene or plagioclase phenocrysts (that host the apatite inclusions) and crystallisation of the apatite microphenocrysts.

The Cl depletion of microphenocryst rims relative to microphenocryst cores could also reflect primary variations in melt composition during apatite crystallisation, or re-equilibration of the microphenocrysts with the partially degassed matrix melt. The variability in halogen contents of apatites open to the matrix, and the small-scale zoning observed when inclusions are trapped adjacent to glass, indicates relatively rapid halogen diffusion in apatite. However, Cl zoning in the microphenocrysts is typically more diffuse than that seen in the partially enclosed crystals, and occurs on similar scales in all crystallographic orientations, whereas halogen diffusivities are strongly anisotropic

(Brenan, 1994). This suggests that the microphenocrysts do in fact record primary growth zoning and not partial re-equilibration.

5.3. Behaviour of sulphur

The population of apatite analyses records a wide spread of sulphur concentrations and there is no statistically significant difference in S content between microphenocrysts and inclusions. However, the X-ray mapping shows that apatite microphenocryst cores are enriched in sulphur relative to the rims, with minor but detectable fluctuations between core and rim in some grains (see Fig. 4). Although early-formed sulphide inclusions are occasionally found in the cores of magnetite and pyroxene phenocrysts, no sulphides are found in the groundmass and this is consistent with the relatively high measured oxygen fugacity of $+1 < \Delta\text{NNO} < +2$ (Andrews, 2014; Singer et al., 2014). This suggests that sulphur is not compatible in any late-crystallising phase in these magmas, and therefore that the decrease in sulphur contents in apatite rims must indicate either a decrease in sulphur concentration in the melt resulting from degassing, or a decrease in the partition coefficient $D_{\text{S}}^{\text{ap-m}}$ due to a change in conditions in the magma. The S partition coefficient for apatite depends on oxygen fugacity (Peng et al., 1997), melt sulphur content and temperature (Parat and Holtz, 2004, 2005). At Santiaguito, we have no evidence for strong changes in magma oxygen fugacity, which is relatively high (estimates range from NNO + 0.5 to NNO + 2, Andrews, 2014; Scott et al., 2012; Singer et al., 2014). Temperature variations may have been important during magma fractionation and ascent, given that temperature estimates for the dacites are 860–885 °C but 925–1040 °C for the basaltic andesite (Singer et al., 2014). However, $D_{\text{S}}^{\text{ap-m}}$ increases with decreasing temperature (Parat and Holtz, 2004, see later), so cooling during fractionation would have the effect of increasing the S content of apatite in equilibrium with the melt, resulting in reverse zoning instead of the observed normal zoning. We therefore conclude that for the most part, the volatile contents of apatite at Santiaguito are related to changes in melt volatile concentration and degassing.

5.4. Quantification of pre-eruptive volatile contents

We used published apatite-melt partition coefficients to estimate pre-eruptive melt volatile concentrations from the analysed apatite compositions. Apatite inclusions in the phenocryst phases are essentially protected from the external melt environment and should therefore retain a reliable record of their original volatile contents, as long as they are not in contact with any melt pockets (see above; Fig. 4). To determine the volatile concentrations in the melt prior to ascent and degassing, we take representative compositions of apatite inclusions and the cores of microphenocrysts (Table 3). Volatile concentrations in the melt after decompression and immediately prior to extrusion are derived from matrix glass compositions.

5.4.1. Sulphur

We estimated $D_{\text{S}}^{\text{ap-m}}$ by first calculating the apatite saturation temperature (i.e., the temperature at which apatite appears on the liquidus), following Piccoli and Candela (1994) and Dietterich and De Silva (2010):

$$\text{AST}(K) = \frac{(26400 \cdot C_{\text{SiO}_2}^{\text{AST}} - 4800)}{12.4 \cdot C_{\text{SiO}_2}^{\text{AST}} - \ln \left(\frac{C_{\text{P}_2\text{O}_5}^{\text{AST}}}{1 - \frac{X}{100}} \right)} - 3.97 \quad (1)$$

where AST is the apatite saturation temperature; $C_{\text{SiO}_2}^{\text{AST}}$ and $C_{\text{P}_2\text{O}_5}^{\text{AST}}$ are the weight fractions of SiO₂ and P₂O₅ in the melt at the point of apatite saturation, and X is the fractional crystallinity of the magma at the point of apatite saturation. In the Santiaguito magmas there are

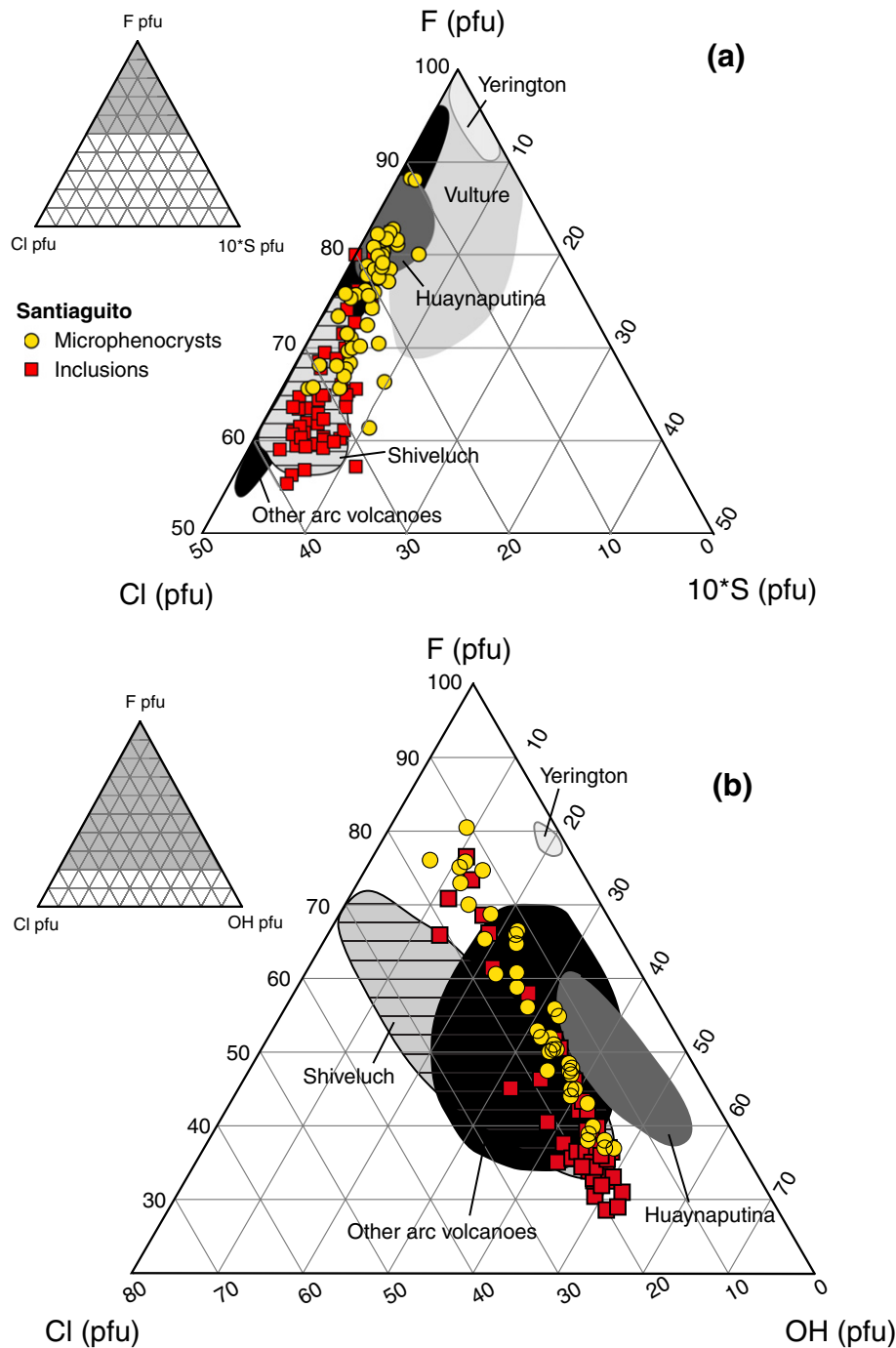


Fig. 3. Ternary diagrams showing (a) S, F, Cl and (b) F, Cl, OH volatile compositions of apatite inclusions (squares) and microphenocrysts (circles) from Santiaguito, expressed as ions per formula unit, with sulphur contents $\times 10$ for ease of comparison. Also shown are fields for other subduction-related systems: Shiveluch Volcano, Kamchatka (Humphreys et al., 2006b), Huaynaputina, Peru (Dietterich and de Silva, 2010), Monte Vulture, Italy (Liu and Comodi, 1993) and Yerington batholith (Streck and Dilles, 1998). 'Other arc volcanoes' (black field) are as reported in Webster et al. (2009), and comprise Krakatau, Indonesia; Pinatubo, Philippines; Mt St Helens, Washington; Santorini, Greece; Lascar, Chile; and Bishop Tuff, California. Insets highlight in grey the sections shown in the main figures.

abundant apatite inclusions in phenocryst phases including plagioclase, pyroxene and Fe-Ti oxides, which suggests that apatite saturation occurred relatively early. This is also supported by the lack of significant P_2O_5 enrichment in the bulk rock compositions (generally < 0.25 wt% P_2O_5 , see Scott et al., 2013). We therefore assume that $C_{SiO_2}^{AST}$ and $C_{P_2O_5}^{AST}$ are equivalent to representative bulk rock compositions (~ 62 – 65 wt% SiO_2 and 0.21 – 0.23 wt% P_2O_5 , Scott et al., 2013). We also infer from the abundance of apatites included in phenocrysts that X may be rather low, and must certainly be less than ~ 0.3 (the proportion of phenocrysts observed in the samples on eruption, Scott et al., 2012,

2013). This range of parameter values gives a range of calculated $AST = 897$ – 987 °C (with 'preferred' values in the range 897 – 963 °C, based on the observation of abundant apatite inclusions within phenocrysts including both plagioclase and pyroxene, leading to the assumption that a reasonable upper limit for the magma crystallinity at apatite saturation is $X = 0.15$, i.e., half of that on eruption). These estimates are at the upper end of (or slightly higher than) temperature estimates for the more evolved magmas (e.g. amphibole-plagioclase geothermometry, 840 – 950 °C, Scott et al., 2012; two-oxide temperatures, 860 – 885 °C, Andrews, 2014; Singer et al., 2014), and at the

lower end of temperature estimates for the basaltic andesite (925–1040 °C, pyroxene and two-oxide thermometry, [Singer et al., 2014](#)).

We then used the empirical relationship obtained by [Peng et al. \(1997\)](#) for the El Chichón trachyandesite to determine a partition coefficient for sulphur:

$$\ln D = \frac{21130}{AST(K)} - 16.2 \quad (2)$$

which gives D_{S}^{ap-m} of 2.4–6.4 for the ‘preferred’ apatite saturation temperatures (897–963 °C). These experimental data were acquired at more oxidising conditions (equivalent to the MnO–Mn₃O₄ to MH buffers) than the Santiaguito magma, and at more appropriate fO_2 conditions D_{S}^{ap-m} would be slightly reduced, by perhaps a factor of 2 ([Peng et al., 1997](#)). In contrast, the strong increase of D_{S}^{ap-m} with decreasing temperature ([Peng et al., 1997](#)) means that cooling during fractionation would result in increasing S contents of apatite in equilibrium with a melt of constant composition, resulting in reverse zoning.

Using D_{S}^{ap-m} of 2.45–6.4, combined with our measured compositions of apatite inclusions (1656 ± 687 ppm) predicts melt sulphur concentrations in the range 151–957 ppm S. Apatite microphenocryst cores ($1396 \text{ ppm} \pm 804$) give melt concentrations of 92–899 ppm S. In comparison, measured matrix glass concentrations were generally low, <360 ppm S ([Table 2](#)). This suggests that the apatite compositions are a reasonable reflection of coexisting melt sulphur compositions, at least if temperatures are in the lower part of our range (leading to higher partition coefficients). Many of the apatites show systematic zoning, commonly with sulphur-poor rims. It seems unlikely that this is a result of changing temperature during crystallisation, as this would require significant heating (to 940–1100 °C) to crystallise apatite with the lowest observed rim S concentrations (~400 ppm) without any change in melt concentration. It is possible that interaction with mafic magma at depth in the volcanic system could cause such a heating effect; however it seems more likely that the apatites may record syn-eruptive sulphur loss related to degassing.

5.4.2. Fluorine and chlorine

To determine Cl and F concentrations in the melt we used empirical partition coefficients determined for hydrous silicic melts (65–71 wt%

SiO₂) in equilibrium with melt and a fluid phase at 200 MPa, 900–924 °C and NNO to NNO + 2.1 ([Webster et al., 2009](#)). These parameters are a good match for the estimated magma storage conditions at Santiaguito, although true ternary F–Cl–OH exchange coefficients would be more strictly appropriate than apparent partition coefficients. The data of [Webster et al. \(2009\)](#) show that X_F^{ap} increases with increasing F and decreasing Cl concentration in the melt; X_F/X_{Cl} (ap) increases linearly with X_F/X_{Cl} (m), with X_F/X_{Cl} (ap) ranging from 0.26–14.9 ([Webster et al., 2009](#)). Their experiments were run at higher Cl contents than the Santiaguito glass, so we only used data from the less Cl-rich experiments that resulted in apatite with ≤ 2 wt% Cl. These give values of apparent D_F^{ap-m} (calculated as $D = F^{ap}/F^m$) from 12.7–37. For the same experiments, equivalent values of D_{Cl}^{ap-m} range from 1.0–3.5.

Using mid-range values for apparent partition coefficients D_F^{ap-m} ($D = 25$) and D_{Cl}^{ap-m} ($D = 2.25$), the apatite microphenocryst compositions indicate melt halogen concentrations in the range 0.06–0.11 wt% F and 0.38–0.53 wt% Cl; apatite inclusions give melt halogen concentrations of 0.04–0.08 wt% F and 0.46–0.60 wt% Cl. Given the full variation in the partitioning data, the possible range of melt concentrations is large, more like 0.04–0.17 wt% F and 0.29–1.19 wt% Cl ([Table 3](#)). This range is consistent with the low measured glass F compositions (lower than the detection limit for at ~0.35 wt% F) and suggests that there has not been significant degassing of F during magma ascent and crystallisation. In contrast, melt inclusions have 700–1600 ppm Cl ([Balcón-Boissard et al., 2010](#)), which is substantially lower than the concentrations predicted from our apatite compositions; our matrix glasses analyses show even lower Cl contents ([Table 2](#)). This result is similar to that of previous studies (e.g. [Boyce and Hervig, 2009](#); [Webster et al., 2009](#)), which also found anomalously high apatite-based estimates for pre-eruptive melt Cl (but not F) concentrations when compared to melt inclusions.

It has been suggested previously that a discrepancy between melt inclusion Cl contents and those calculated from apatite could be due to exsolution of a low-density aqueous vapour from a higher density single-phase fluid coexisting with the magma during ascent ([Webster et al., 2009](#)). Subsequent segregation of the low density vapour would result in increasing salinity of the remaining saline fluid and re-equilibration of apatite to more Cl-rich compositions ([Webster et al., 2009](#)). There is no direct evidence of the presence of a high density

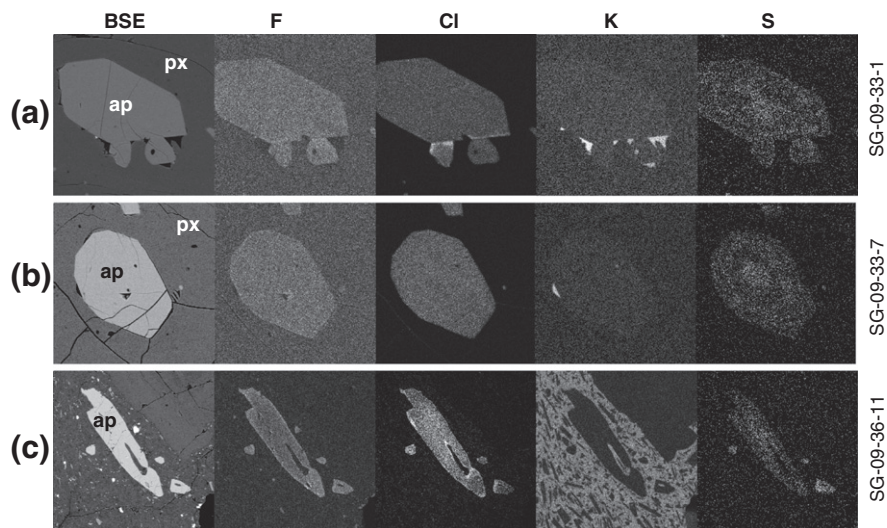


Fig. 4. Back-scattered electron SEM images and X-ray maps showing volatile element zoning in apatite inclusions and microphenocrysts from Santiaguito Volcano. (a) SG-09-33-1, three inclusions in pyroxene host. Small filaments of melt are trapped at the lower margin of the inclusion, clearly visible in the K map. Re-equilibration of apatite Cl contents with the melt is apparent. The inclusion also has a sulphur-rich core. (b) SG-09-33-7, single inclusion within pyroxene host. There is no small-scale re-equilibration as in (a) despite the presence of a small melt pocket, but still clear S-enrichment in the core of the inclusion. (c) SG-09-36-11, microphenocryst with melt embayment. Both F and Cl show clear core-rim zoning, with higher volatile contents at the rim. There is also short lengthscale, high-amplitude zoning in Cl at the rim of the melt embayment. The microphenocryst shows slight S enrichment in the core.

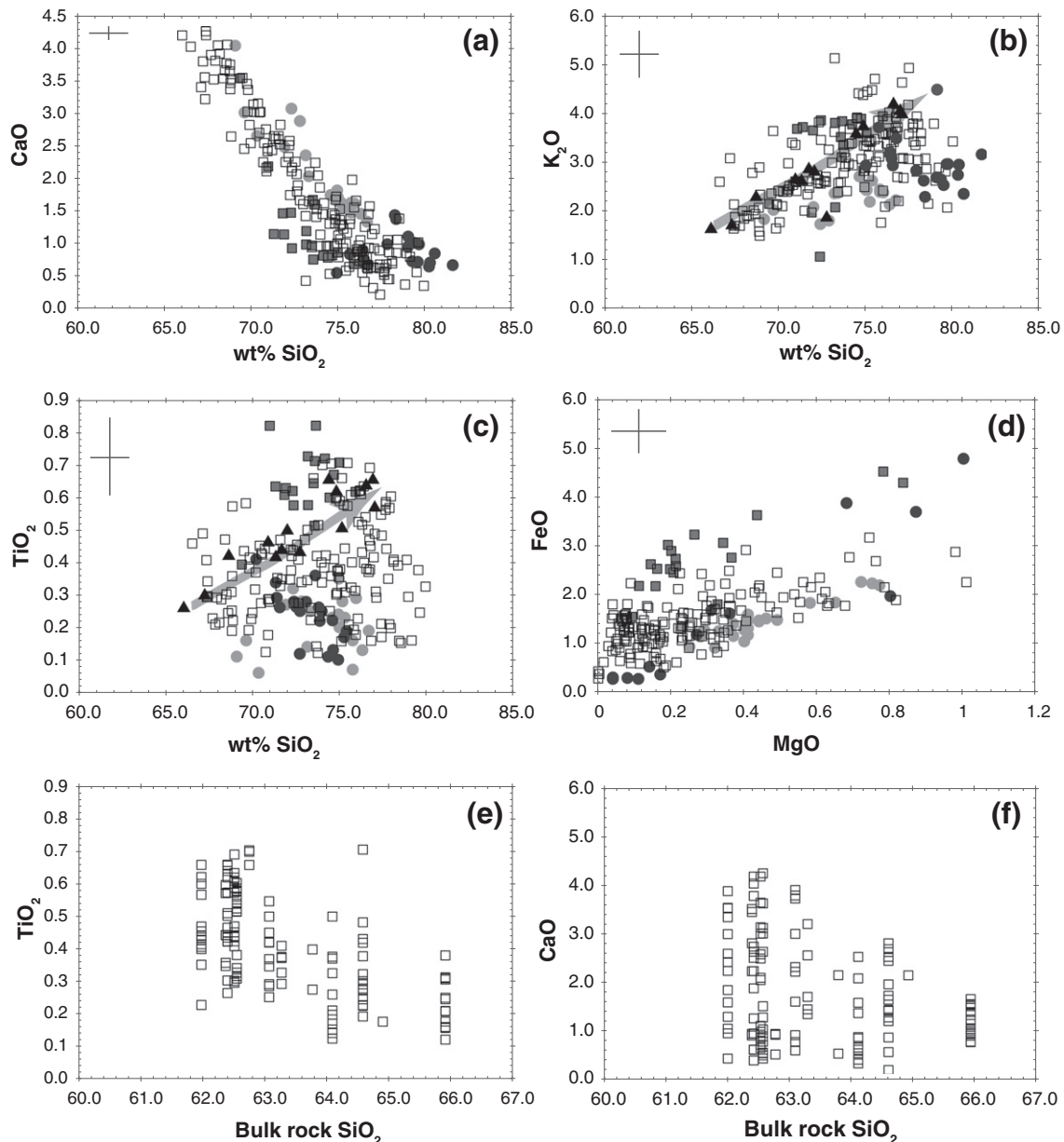


Fig. 5. Glass compositions from Santiaguito Volcano (open squares, matrix glasses from Scott et al., 2013; filled squares, glomerocryst glass from this study) together with published plagioclase-hosted melt inclusion data from the basaltic andesite (dark filled circles) and pumice (light filled circles) of Santa María, 1902 (Singer et al., 2014). Black triangles and underlying grey arrow in (b) and (c) illustrate relatively clear trends seen for individual samples (here, SG-09-03, see Table 2). (a) CaO shows a clear decrease with increasing SiO₂. (b) K₂O contents increase with increasing SiO₂ but the most evolved samples (with ~75 wt% SiO₂) have lower concentrations. (c) TiO₂ shows the same pattern as K₂O but more exaggerated. (d) Good correlation between Fe and Mg contents. (e) and (f). TiO₂ and CaO concentrations decrease with increasing bulk rock SiO₂ content.

saline fluid at Santiaguito, although the melt Cl contents predicted from apatite may be approaching the concentration at which a dense fluid could become stable (Signorelli and Carroll, 2001; Webster, 2004). However, the process described by Webster et al. (2009) should result in partial equilibration of the larger apatite grains to leave Cl-rich rims, whereas Cl-poor rims are observed. It is unlikely that the discrepancy between predicted and observed melt Cl concentrations is the result of apatite growing at volatile-undersaturated conditions, because previous melt inclusion studies demonstrate Cl–H₂O loss during magma ascent (Singer et al., 2014; Villemant et al., 2003). We can also rule out early crystallisation in a higher temperature, less fractionated melt, as this would result in a lower $D_{\text{Cl}}^{\text{ap-m}}$ (Webster et al., 2009) and hence higher melt Cl contents for a given apatite composition. This leaves the most obvious explanation for the low Cl contents of the matrix glasses being that the matrix has substantially degassed, resulting in

loss of Cl into the vapour phase during ascent. This is supported by the covariation of Cl and H₂O in melt inclusions and residual matrix glasses of Plinian clasts (Villemant et al., 2003).

5.5. The ‘petrologic method’ using apatite

The pre-eruptive dissolved volatile concentrations predicted from apatite can be used to estimate the flux of SO₂, HF, and HCl from Santiaguito, in the same way that the ‘petrologic method’ is commonly used with melt inclusions (e.g. Dietterich and de Silva, 2010; Thordarson et al., 1996; Wallace, 2005). First, the amount of volatiles degassed is constrained using the difference between apatite-based estimates of pre-eruptive melt volatile concentrations (0.29–1.19 wt% Cl, 0.03–0.17 wt% F, 218–676 ppm S, Table 3) and matrix glass volatile concentrations. We use the upper estimates of

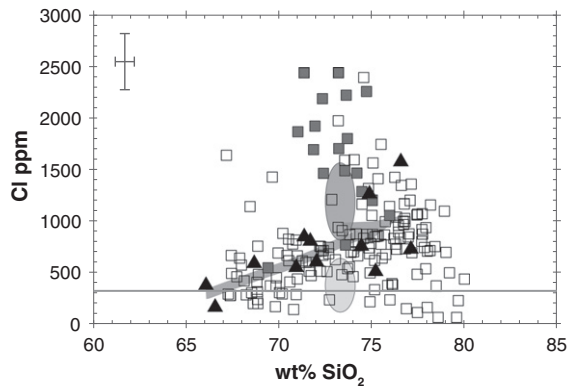


Fig. 6. Cl contents of matrix glasses (open squares) and glomerocryst glasses (filled squares) from Santiaguito Volcano plotted against the SiO₂ content of the host bulk rocks. Cl concentrations follow a similar pattern to K₂O and TiO₂ (see Fig. 5), increasing and then decreasing after ~75 wt% SiO₂. Error bars shows ± 1 sigma analytical uncertainty on the analyses; horizontal line represents the detection limit (~300 ppm Cl). Two grey ovals represent the range in composition of matrix glasses and melt inclusions from the 1902 Plinian eruption (dark grey) and later dome rocks (light grey) as measured by electron microprobe (Balcone-Boissard et al., 2010; Villemant et al., 2003).

matrix glass concentrations (0.03 wt% F from Balcone-Boissard et al., 2010; 0.11 wt% Cl and 358 ppm S, Tables 2 and 3) in order to obtain a minimum estimate of the extent of degassing. The total volume of magma erupted at Santiaguito since 1922 is 1.1–2 km³ (Ebmeier et al., 2012; Harris et al., 2003; Scott et al., 2013); using a typical dacite magma density of 2500 kg m⁻³ gives a total erupted mass of 2.75×10^{12} – 5×10^{12} kg. Assuming a mean phenocryst content of ~30% (Scott et al., 2012), this equates to 1.9 – 3.5×10^{12} kg melt. Thus the total mass of volatiles emitted since 1922 is up to 2.8×10^9 kg S, 2.4×10^9 – 4.5×10^{10} kg Cl and up to 6.3×10^9 kg F (Table 3).

This suggests time-averaged SO₂ emissions of up to 157 tonnes/day (Table 3), which is similar to previous estimates based on sporadic field measurements (between 20 and 960 tonnes/day, see Table 4, Andres et al., 1993; Holland et al., 2011; Rodriguez et al., 2004). The same method suggests time-averaged estimates of 74–1380 tonnes/day HCl and up to 196 tonnes/day HF (Table 3). These results give gas species ratios of HF/SO₂ ~ 1.25, and HCl/SO₂ ~ 0.5–8.8. Because the melt Cl

concentrations calculated from apatite are rather high compared with melt inclusions (see earlier), we consider that the lower HCl flux values are probably more reliable. There are no published field-based estimates of Santiaguito's halogen emissions, so we are unable to compare this with independent constraints on HCl flux from the volcano. It is not trivial to compare long-term petrological estimates with spot measurements of gas emissions at any individual volcano, primarily because gas fluxes may be highly variable in time, depending on the level of volcanic activity. For example, the HCl flux (and consequently the HCl/SO₂ ratio) at arc volcanoes is typically related to direct magma extrusion and falls to very low levels during periods of non-extrusion (e.g. Edmonds et al., 2001). Spot field measurements for SO₂ at Santiaguito are highly variable in time and also appear to depend on whether there is active extrusion at the lava dome (Holland et al., 2011; Rodriguez et al., 2004).

A well-monitored volcanic system that also shows long-term dome-building activity is Soufrière Hills Volcano, Montserrat. Cl is degassed from the andesite magma during extrusion but sulphur is mostly supplied by deeper degassing of unerupted mafic magma (e.g. Edmonds et al., 2001, 2010). Soufrière Hills Volcano has emitted approximately $4.0 \pm 0.6 \times 10^9$ kg sulphur during the course of the prolonged 1995–2011 dome-forming eruption, including both SO₂ and H₂S (Edmonds et al., 2014). Similarly to Santiaguito, SO₂ emission rates have been highly variable during the eruption (e.g. 42 to >1900 tonnes/day during 1996–1997, Young et al., 1998), with long-term time-averaged SO₂ emission rates ~600 tonnes/day SO₂ (Christopher et al., 2010; Edmonds et al., 2014), approximately twice the upper estimate for the SO₂ flux emitted at Santiaguito (see Table 4). At Soufrière Hills Volcano, the HCl/SO₂ ratio is <0.3 during pauses, >1 (up to ~10) during active extrusion (Christopher et al., 2010; Edmonds et al., 2014), with HCl emission rates of >400 tonnes/day during dome-building and <80 tonnes/day during pauses in extrusion (Edmonds et al., 2002). The inferred HCl flux at Santiaguito is therefore in line with that observed during dome growth at Soufrière Hills. However, the HCl/SO₂ ratios at Santiaguito extend to higher values than Soufrière Hills Volcano. One explanation for this is the apparently substantially lower SO₂ fluxes at Santiaguito. This may reflect differences in the details of the deep plumbing system (a substantial proportion of the SO₂ supply at Soufrière Hills is contributed by unerupted mafic magma, whereas the long-term petrologic estimates for Santiaguito consider only sulphur degassed from the magma that is erupted; alternatively mafic magma

Table 3
Details of "petrologic method" calculations using apatite and matrix glass compositions.

		F wt%		Cl wt%		S, ppm	
		Avg	$\pm 1 \sigma$	Avg	$\pm 1 \sigma$	Avg	$\pm 1 \sigma$
Apatite (microphenocrysts)		1.98	0.45	1	0.11	1396	804
Apatite (inclusions)		1.5	0.46	1.19	0.15	1656	687
<i>Melt, from apatite microphenocrysts[€]:</i>							
Calculated melt (using low D [€])		0.166	0.043	1.02	0.17	570	302
Calculated melt (mid-range D)		0.085	0.022	0.453	0.076		
Calculated melt (using high D)		0.057	0.015	0.291	0.049	218	125
<i>Melt, from apatite inclusions[€]:</i>							
Calculated melt (using low D)		0.118	0.036	1.19	0.15	676	263
Calculated melt (mid-range D)		0.06	0.018	0.529	0.067		
Calculated melt (using high D)		0.041	0.012	0.34	0.043	259	109
Matrix glass (*§)		0.03		0.083	0.033	135–358	§
Mass degassed, as wt% of melt	min	0		0.126		0	
	max	0.179		1.290		804	
Mass melt erupted since 1922, kg		1.9×10^{12} – 3.5×10^{12} (see text for details)					
Mass F, Cl, S degassed, kg	min			2.4E + 09			
	max	6.3E + 09		4.5E + 10		2.81E + 09	
Avg tonnes/day (from 1922–2014)	min			74			
	max	196	HF	1382	HCl	157	SO ₂

[€] For D values see text.

* Balcone-Boissard et al. (2010) matrix glass concentrations used for F.

§ Most glasses have sulphur bd so use detection limit (135 ppm) as lower limit here. Upper limit is maximum detected concentration (see Table 2).

§ Average detected matrix glass concentrations used for Cl, Table 2.

Table 4
Estimated volatile flux from Santiaguito, based on apatite analyses (this study), with directly measured flux from other volcanoes for comparison. Halogen/ SO₂ ratios for Santiaguito were calculated from the petrological data as described in the text. For Mount St Helens, reported flux data were used to calculate halogen/ SO₂ ratios. § SO₂ fluxes show short-term variations from 30–154 tonnes/day within individual cycles of explosion and repose.

		SO ₂ (tonnes/day)	HF / SO ₂ (by mass)	HF (tonnes/day)	HCl / SO ₂ (by mass)	HCl (tonnes/day)	References
Santiaguito, Guatemala	This study – petrologic method using apatite and matrix glass	Up to 157	1.25	Up to 196	0.5–8.8	74–1382	
Santiaguito, Guatemala	Persistent degassing, average rates	30–210	-	-	-	-	Andres et al. (1993)
Santiaguito, Guatemala	Periods of eruption, average rates	60–960	-	-	-	-	Andres et al. (1993)
Santiaguito, Guatemala	Persistent degassing (period of higher lava extrusion rate)	20–190	-	-	-	-	Rodriguez et al. (2004)
Santiaguito, Guatemala (§)	Daily average across complete explosion-repose cycles	55–85	-	-	-	-	Holland et al. (2011)
Fuego, Guatemala	Persistent degassing	280–340	-	-	-	-	Rodriguez et al. (2004)
Pacaya, Guatemala	Persistent degassing	350–2380	-	-	-	-	Rodriguez et al. (2004)
Tacana, Guatemala	Persistent degassing	30	0.015–0.019	-	0.11–0.13	-	Rodriguez et al. (2004)
Popocatepetel, Mexico	Dome-building		0.16		0.35		Love et al. (1998)
Lascar, Chile	Dome-building		0.008–0.14	2	0.06–1.0	14	Mather et al. (2004)
Mount St Helens, Washington, USA	Dome-building	14–240					Edmonds et al. (2008), Gerlach et al. (2008)
Soufrière Hills, Montserrat	Dome-building	42–1933	0.007	39	0.3–12.6	>400–6000	Allen et al. (2000), Edmonds et al. (2001, 2002), Young et al. (1998)
Sakurajima, Japan	Dome-building		0.009–0.015		0.14–0.33		Mori and Notsu (2003)

supply rates at Santiaguito may differ from those at Soufrière Hills). The mismatch between apatite and melt inclusion Cl contents is another source of uncertainty here.

5.6. Apatite: its potential for tracking volcanic degassing

There is considerable potential for using apatite to infer magmatic volatile contents and time-averaged gas emissions for S, F, and Cl, as an alternative to melt inclusion-based methods (e.g. Huaynaputina, Peru, [Dietterich and de Silva, 2010](#)). This may prove particularly useful when direct emissions measurements are unavailable, for historic and prehistoric eruptions, and for comparison with intermittent gas sampling methods, which are typically highly variable in time. However, there still remain significant problems associated with using apatite to infer magmatic volatile concentrations, not least in estimating the point at which apatite started to crystallise. One of the most significant problems is uncertainty over the presence and composition of any fluid(s) coexisting with the melt, coupled with a lack of constraints on the ultimate fate of a brine phase, if present. This uncertainty still exists for melt inclusion studies, but for apatite the problem is trickier because of the strong dependence of apatite halogen contents on fluid composition ([Webster et al., 2009](#)). More focus is required on demonstrating possible fluid immiscibility, including documenting the presence of multiple fluid bubbles in melt inclusions, as well as the composition of fluid inclusions. Melt inclusions are useful to constrain whether there has been volatile saturation in the melt.

Additional problems arise when there is also substantial variability in the compositions of apatite. Apatite inclusions and microphenocrysts presented here show considerable compositional variability, with 1 relative standard deviation ~12–15% for Cl, 25–30% for F and 40–50% for S. For the most part this variability appears to be real, although improved precision (e.g. by use of ion microprobe techniques) would be helpful, as would direct analysis of OH for accurate determination of Cl/OH and F/OH ratios. Significant variability between grains means that it is difficult to demonstrate that apatites represent equilibrium compositions, as well as to determine which values are truly representative of pre-eruptive magmatic conditions, and at what conditions. Syn-eruptive diffusive equilibration of microphenocrysts with degassed matrix glass can, in principle, be distinguished from crystallisation effects by considering the lengthscale and anisotropy of compositional gradients. Accurate and precise knowledge of magmatic conditions (*f*O₂, pressure and temperature) is required for sensible choice of partition coefficients, and thermodynamic calculations may help in this regard. Finally, application of apatite as a tracer of magmatic volatiles would be enhanced by knowledge of partitioning characteristics of all the volatiles (including OH and C), as well as direct determination of these elements in both apatite and melt.

6. Conclusions

The eruption of Santiaguito volcano, Guatemala, is highly active and amongst the longest-lived of its kind in the world. However, due to its location, climate and the surrounding terrain there are few constraints on gas emissions from this volcano. Apatite in Santiaguito lavas retains evidence of volatile zoning, recording loss of sulphur and chlorine between early entrapment of inclusions and crystallisation of microphenocryst rims. This is likely related to degassing of Cl and S from the magma together with aqueous vapour. Pre-eruptive melt volatile concentrations were determined from the apatite compositions using published partition coefficients. These were used, together with matrix glass compositions, to derive time-averaged estimates of SO₂, HF, and HCl fluxes from Santiaguito. These results indicate time-averaged fluxes of up to 157 tonnes/day SO₂, up to 196 tonnes/day HF, and 74–1380 tonnes/day HCl. Estimated ratios are HF/SO₂ ~ 1.25, and HCl/SO₂ 0.5–8.8. These fluxes are in line with estimates from other arc volcanoes; however the

uncertainties are large and additional work is needed to constrain volatile exchange coefficients between apatite and melt \pm fluid(s), including in volatile-undersaturated systems, as well as direct analysis of OH in both apatite and melt.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.lithos.2015.07.004>.

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